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16. ABSTRACT The report describes the facility construction and gives results of preliminary tests for a project that seeks a fundamental understanding of the factors and conditions that cause the production of environmental pollutants in synthetic fuels processes. Tasks include: operation of a laboratory-scale coal gasification facility; collection and chemical analysis of effluent stream samples; compilation and analysis of resulting data; and evaluation of these data. The experimental system operates successfully and reliably at gasification temperatures up to 1370 K, pressures up to 1.2 MPa, and gas generation rates of about 20 standard liters/min. Analytical chemical methods, developed for analysis of effluents from these coal gasification tests, promise to achieve the required levels of sensitivity and extent of compound identification and quantitation. For example, liquid chromatography/mass spectrometer/computer analysis is used to quantitate organic compounds. The major pollutant classes are benzene and its substituents, thiols and sulfides, phenols, fused polycyclics, sulfur heterocyclics, and inorganic sulfur compounds.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Polycyclic Compounds	Pollution Control	13B
Fuels	Sulfur Heterocyclic Compounds	Stationary Sources	21D
Coal Gasification		Synthetic Fuels	13H
Chemical Analysis		Fuel Production	07D
Benzene		Sulfides	07C
Thiols		Fused Polycyclics	
Phenols			

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ABSTRACT

This project seeks to develop a fundamental understanding of those factors and conditions that cause the production of environmental pollutants in processes oriented to the production of synthetic fuels. The information so generated is to aid in the control of the potentially hazardous material which may be produced in the fossil fuels conversion plants utilized in coming years. The project involves the operation of a laboratory coal gasification system, the collection and chemical analysis of effluent stream samples, the compilation and analysis of the resulting data, and the evaluation and comparison of these data.

The experimental work has included the design, fabrication, and preliminary operation of the laboratory gasifier to represent conditions which may be utilized in commercial plants for coal conversion to synthetic fuel gas. An experimental program has also been developed for the chemical analysis of organic compounds produced in the reaction process. Sampling procedures as well as specific chemical analysis techniques have been studied, developed, and implemented for utilization in this work. The research has focused on three major product categories:

1. major gas products (permanent gases);
2. volatile organic compounds (low-level gas components);
3. low volatile organic compounds (tar components).

Screening tests are underway to establish acceptable operating conditions for the system, to identify the various organic compounds of interest to the study, and to determine coal types for further study. These will be followed by parametric tests to characterize the compounds contained in the synthesis reactor effluent stream as a function of the reactor operating parameters. Kinetic tests are also planned to determine the rates of formation of various pollutants of significance and the possible application of this information to the reduction of pollutant

formation in operating systems. The engineering studies involve the planning of the various test runs included in this experimental project and the interpretation of the results thus far obtained from the various experimental tests. The data are utilized to assess the nature and extent of various environmental hazards resulting from specific compounds produced during synthetic fuels operations.

An operating experimental system has been achieved which functions both successfully and reliably. Analytical chemical methods have been developed which promise to achieve the levels of sensitivity and the extent of compound identification and quantitation required to meet the objectives of this project. This facility has the capability for solid fuel gasification at temperatures ranging up to about 1370°K (2000°F), pressures to about 1.2 MPa (300 psia), and product gas generation rates of the order of 20 standard liters/min. Glass sample bulbs are used to collect gases for subsequent gas chromatographic analysis. In addition, Tenax and XAD-2 resin cartridges are used to adsorb volatile organic compounds for subsequent analysis on a gas-liquid chromatography/mass spectrometer/computer analysis system. The organic compounds of low volatility, which constitute the tars and organic materials contained within the aqueous condensate, represent an important class of materials for identification and quantitation. These samples are partitioned into organic acids, organic bases, and PNA hydrocarbons for subsequent analysis.

The gas chromatography/mass spectroscopic analysis of the organic samples collected from coal tests typically reveal the presence of more than 200 compounds. Equally large numbers of compounds appear to be present in the less volatile samples collected from the tar and water condensate trap. A specific list of organic compounds for identification and quantitation has been developed to reduce the task of organic compound characterization to one of practical proportions. These compounds include benzene, naphthalene, acenaphthene, pyrene, fluorene, fluoranthene, phenol, cresol, pyridine, and dibenzofuran.

Future work in this project will be concerned with parametric studies which examine the generation and control of potential pollutants in coal gasification under various operating conditions. The parameters to be considered for investigation include coal type, grind size, steam and air (oxygen) flow rates, coal pretreatment, bed depth, temperature, pressure, and reactant residence times. It is also anticipated that the reactor can be operated in both the fixed bed and fluidized bed configurations. Thermodynamic and reaction kinetic studies are intended to describe the pollutant generation process as well as to attempt to determine (1) the mechanism of the formation of various pollutant materials, (2) the rate of production of each of the pollutant materials, and (3) the influence of various operating conditions upon the level of each pollutant in the effluent stream. The information being generated provides the basis for the assessment of the hazard potential of the effluents from coal gasification processes and is intended for use to determine the extent to which these hazards may be reduced.

This report is submitted to describe facility construction and preliminary tests performed in partial fulfillment of Research Grant R804979 by the Research Triangle Institute under sponsorship of the U.S. Environmental Protection Agency. This report covers a period from November 1976 through April 1978.

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LIST OF ABBREVIATIONS AND SYMBOLS

A_o	--	frequency (pre-exponential) factor
amu	--	atomic mass units
BKG	--	background compound
ΔE_a	--	activation energy for reaction
EPC	--	estimated permissible concentration
eI	--	standard (reference) compound
e.v.	--	electron volts
FID	--	flame ionization detector
FPD	--	flame photometric detector
GC	--	gas chromatographic column
GLC	--	gas-liquid chromatographic column
k	--	reaction rate constant
K	--	reaction equilibrium constant
M	--	mesh (screen size)
MATE	--	minimum acute toxic effluent
MERC	--	Morgantown Energy Research Center
MS	--	mass spectrometer
p	--	partial pressure
PERC	--	Pittsburgh Energy Research Center
PNA	--	polynuclear aromatic hydrocarbon
ppm	--	parts per million, by volume
R	--	ideal-gas law constant
RTI	--	Research Triangle Institute
S	--	surface area for reaction
SCOT	--	support coated open-tube column
STP	--	standard temperature and pressure

T	--	temperature, °K
TC	--	thermal conductivity detector
Tenax	--	*polymer adsorbent*
tent	--	tentative
TIC	--	total ion current
X	--	fractional chemical conversion
XAD-2	--	Amberlite resin adsorbent

NOTE: Standard metric units and abbreviations are provided throughout this report.

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Denny Wagoner, Santosh Gangwal, Peter Groshe and Robert Denyszyn developed and implemented the gas sampling system as well as the associated chemical analysis procedures. The adsorbent cartridge sampling procedures, the tar partitioning scheme and the associated chemical analysis data interpretation work were all performed by Charles Sparacino, Ruth Zweidinger, Sarah Willis, Jesse McDaniel and Douglas Minick. Significant mass spectrometric support activities were contributed by Kenneth Tomer, William Hargrove and David Rosenthal.

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1.0 INTRODUCTION

The Research Triangle Institute has undertaken a project directed toward understanding the nature and extent of the production of environmental pollutants in synthetic fuels processes. This project sponsored by the Industrial Environmental Research Laboratory/Research Triangle Park of the U.S. Environmental Protection Agency is in its second year of a five-year project period.

The overall purpose of this program is twofold: (1) to develop a fundamental understanding of those factors and conditions that cause the production of environmental pollutants in synthetic fuels processes; and (2) to provide information needed for the control of potentially hazardous material from plants which may be used to produce synthetic fuels in the coming years.

The work to date includes equipment construction, installation, and preliminary experimental testing.[4,17] In addition, initial work has been performed relative to the interpretation of experimental data obtained from a variety of analytical chemical test procedures.[29] After completion of the preliminary testing of the reactor and sampling system and the satisfactory development of analytical chemical tests and methods, the laboratory gasifier system is to be utilized to screen the pollutants from a variety of coals considered to be candidates for coal gasification within the United States. These screening tests will be concerned with the characterization of the chemical constituents of the reactor effluent stream as a function of the input coal utilized and the reactor operating conditions. An additional aspect of the experimental program involves the study of the fate, rate of conversion and mechanism of formation of the pollutants of significance that are generated via the coal gasification process. It is hoped that the results of this study will permit the reduction of pollutant formation in operating reactor systems.

Additional analytical work which is to be a part of the overall project effort involves the utilization of results of the screening tests to (1) project human exposure to discharges from alternative coal gasification plants and (2) establish priority ratings for the various pollutants based on the extent to which projected exposures are hazardous.

During the first year of this project, a coal gasification laboratory was designed and made operational. Tests have been completed for a low volatile, noncaking char to check out the operating system. In addition, a series of preliminary experiments utilizing FMC char and Illinois No.6 coal has been performed.

A sampling system made of stainless steel was first used. This sampling system has since been replaced by a glass system which offers greater versatility for use in the sampling process. Gas samples are collected using glass sample bulbs, Tenax adsorbent cartridges and XAD-2 adsorbent cartridges. Samples from the glass bulbs are introduced directly to the inlet system of the gas chromatograph to quantitatively determine the amounts of permanent gases, sulfur species gases and C_1-C_6 hydrocarbons.

Thermal desorption recovers volatile organics from the Tenax cartridges and methylene chloride is used to extract organic compounds from the XAD-2 adsorbents. The samples thus obtained are analyzed using the technique of gas-liquid chromatography/mass spectrometry/computer analysis. A substantial effort is required to achieve an appropriate instrument calibration for these analyses in order to permit the accurate qualitative and quantitative determination of the organic compounds present.

Tars that are collected in a condensate trap are subjected to a solvent partition scheme in order to isolate the compound categories of organic acids, organic bases, polar neutral compounds, nonpolar neutral compounds, PNA hydrocarbons and cyclohexane insoluble material. Various techniques have been studied for the analysis of the organic acids, organic bases and PNA hydrocarbons. These include exclusion chromatography, reverse-phase chromatography, nuclear magnetic resonance analysis and direct probe mass spectrometry. The greatest success has been achieved utilizing capillary chromatography, temperature programming

and GC/MS detection for these low volatile compounds. The direct probe technique of sample introduction to a mass spectrometer operating at low voltage levels has also shown some promise as a chemical analysis technique of value in this study. A working list of specific hazardous compounds has been developed based upon (1) the EPA Effluent Guidelines Division's list of priority pollutants of BAT revision studies (consent decree compounds), (2) minimum acute toxic effluents (MATE) values and (3) known pollutant compounds occurring in relatively high concentrations in the effluent streams. Therefore, the organic compounds that are being identified and quantitatively determined include those which are known hazardous materials or possess potential as environmental hazards in relation to releases to the air, water streams or solid waste depositories.

A number of previous research projects have concerned the chemical analysis of effluents from commercial and/or developmental gasification processes. These include studies on fixed bed, fluidized bed, and entrained bed gasification reactor systems. Uniquely, this study has its focus on a complete evaluation of the chemical and toxic nature of the effluent streams as well as a fundamental understanding of the influence of the reactor operating conditions upon the results achieved. The parametric values of operating conditions for this study, therefore, are selected to characterize the various coal gasification processes currently under development.[18,19]

2.0 CONCLUSIONS, PROBLEM AREAS AND PLANS

An experimental bench-scale investigation has begun which includes the generation, collection, processing, analysis, characterization and evaluation of the pollutants from the gasification of coal. Coal and coal char have been gasified in a fixed bed reactor under selected operating conditions. Particulates, condensates, organic volatile compounds and effluent gases have been collected and processed for characterization and chemical analysis. Analytical chemical measurements include: the ultimate and proximate analyses of the coals, chars and residues; the gas chromatographic analysis of the primary gaseous products; the adsorption and analysis with GLC/MS/computer interpretation of the volatile organic compounds; and the collection, partition, and GLC/MS analysis of the semivolatile (tars and other low volatile organic) compounds.

Primary progress to date includes the equipment assembly and preliminary testing which have led to a number of conclusions. Additional results and recommendations are anticipated after the analysis and evaluation of the data from experiments in this program.

2.1 CONCLUSIONS

The laboratory coal gasification reactor system, which has been constructed, assembled, and operated as a part of this project, can be operated to simulate the primary operating conditions, the gas yield and composition and the tar yield of commercial and developmental coal gasifiers so as to provide a means to study the processes and conditions under which both major and minor pollutants are formed. Data records can be assembled, compiled and stored, representing the operating conditions with such a gasifier as a function of the reaction time and the reactor configuration. To date, the reactor has been operated in the semibatch fixed bed mode. However, it is anticipated that a fluidized bed mode of operation will also be feasible.

Sample collection equipment and procedures have been developed for particulates, semivolatile organic compounds (tars and other low volatile organics), aqueous condensates, volatile organic compounds and primary gaseous effluents. This sampling procedure has been specifically developed to permit a careful analytical determination of the types and quantities of the various compounds present in each of the samples which are collected.

Reliable gas chromatographic techniques have been identified and used on the primary gaseous effluent stream. GLC/MS/computer analysis techniques are being employed for both the volatile organics and the semivolatile organic constituents. The qualitative and quantitative determination of polynuclear aromatic hydrocarbons has been successful up to compounds having five condensed aromatic rings. A partitioning scheme has been perfected for use with the tars collected during the experiments. The major components of the tar acids and tar bases have molecular weights up to 350. The polar and nonpolar neutral compounds have been present in significant quantities up to molecular weights of approximately 450. The PNA fraction has been found to contain a series of compounds resulting in prominent peaks at atomic mass unit intervals of 24 or 26 from 178 to 380. These results correspond to condensed aromatic structures with from 3 to 9 rings. The highest intensity peaks occurred at the atomic mass unit values of 202, 252, and higher, indicating that lesser amounts of the lower molecular weight PNA compounds were present in the sample.

Over nine classes of organic compounds were identified in the gasification reactor effluents that were judged to be potentially hazardous. These include benzene and some of its derivatives, phenol, other phenol-type compounds, and polynuclear aromatic hydrocarbons. Also included were compounds containing the hetero-atoms of sulfur, nitrogen, and oxygen.

A list of 102 specific hazardous compounds has been prepared for use in this study. This includes 42 of the 131 compounds on the EPA Effluent Guidelines Division list of priority pollutants for BAT revision

studies (consent decree compounds). Some 25 hazardous compounds from the list of 102 have been identified in the effluent stream from the coal gasifier. These 25 include 14 of the consent decree compounds.

Of the 102 specific hazardous compounds under study, 21 have previously been identified in effluents from the fixed bed gas producer at the Morgantown Energy Research Center, 39 in the products of various coal liquefaction operations, and 52 in the products of coal coking operations.

2.2 PROBLEM AREAS

Some difficulty was encountered in operating equipment at low flow rates for the steam feed to the reactor. This problem has been effectively alleviated by the proper selection of operating conditions, including the heat rates selected for the three steam generating furnaces. Further, heating rates are needed for the reactor coal bed such that conversion temperatures are at desired levels for both noncaking and moderately caking (agglomerating) coals. This has required that specific attention be paid to the operating temperatures achieved when the external reactor furnace is operating.

Development of chemical analytical techniques for high molecular weight organic compounds occurring at trace levels has been particularly challenging. These methods have been under continual improvement throughout the effort to date. It appears that direct probe techniques utilizing low voltage mass spectrometer operation will permit a characterization of these compounds and that a substantial effort is required for the analysis of each sample on the GLC/MS/computer analysis system. Some consideration has been given to automating the process of compound identification being utilized with this approach.

It has been quite difficult to compile complete information on the potential hazardous effects associated with all of the various compounds that may be associated with the conversion of coal to gaseous products. However, the utilization of toxic information expressed in lethal dose statistics, as well as the literature data on carcinogenic effects of various compounds, are being used. This information has been used in the form of minimum acute toxic effluent (MATE) values.

2.3 FUTURE PLANS

It is anticipated that future experiments to be conducted with the equipment described herein will be divided into three test types: screening tests on various solid fuels representative of those materials having potential for synthetic gas production; parametric tests in which temperatures, pressures, air-to-steam ratios and other operating conditions will be varied to simulate commercial and/or developmental gasification reactors; and kinetic tests aimed at measuring rates of pollutant conversion. The specific operating conditions will be carefully selected based upon the laboratory system operability as defined by equipment design, laboratory experience and the aim to simulate practical gasification conditions. As in commercial and/or developmental gasification reactors, it may be necessary to pretreat some high-volatile coal types in order to successfully operate the gasification reactor with the high caking (agglomerating) coals.

Continuing effort is planned to further develop techniques appropriate to the sampling and chemical analysis of the PNA organic compounds and other trace constituents of the gasification reactor effluent stream. Sample partitioning, high pressure liquid chromatographic techniques and possible sample derivatization methods may be necessary. It is anticipated that chromatographic and mass spectrometric methods will be employed. The automation of the compound identification process would permit a substantial increase in the productivity of this effort.

The automatic collection of operating data, the processing of gas chromatographic data and data storage and retrieval capabilities are being implemented. The data and signal processing system may make it possible to perform data reduction and correlation studies in a routine fashion for at least some of the results to be achieved with the laboratory gasification system.

Correlations of the results of this study are being sought with respect to such parameters as feed type, operating conditions, classes of compounds emitted, characteristic functional groups possessed by the effluents and hetero-atoms present with these compounds. This effort is expected to become more meaningful as more types of solid feed are studied.

3.0 REACTOR AND ACCESSORIES

3.1 EXPERIMENTAL EQUIPMENT

A plan-view sketch of the reactor laboratory in use for this project is shown in Figure 1. Solid fuel feed material is prepared and stored in the laboratory in preparation for each of the gasification tests. Runs to date have included both char and coal feed material with a size of 8 X 16 mesh. A coal charge is placed in the reactor feed hopper which is inside the enclosed high pressure area. The gas storage cylinders provide nitrogen or other permanent gases to the reactor. Deionized water is metered to steam generation furnaces in order to provide a steady flow rate of steam to the reactor. The metering pumps have the capacity to supply from 0.5 to 5.0 kg of water/hour to the reactor.

The reactor system is shown in Figure 2. The reactor is constructed from a nominal 3-inch diameter (7.6 cm), schedule 160, type 310 stainless steel pipe and is approximately 1.2 m in length. Above it is located the coal hopper and coal feed system. This consists of a nominal 2-inch (5 cm) diameter, schedule 40 steel pipe, which is approximately 0.5 m in length. The sight glass joints are connected to the coal feed system with flanges at each end. The sight glass permits the operator to view the descent of solid feed as it is added to the reactor. A pneumatically actuated Jamesbury stainless steel ball valve is located between the feed hopper and the reactor. Once the coal solids have been admitted into the reactor space, a bed of solids exists within the reactor which is supported by an aluminum flow distributor.

Steam and other gases are introduced into the bottom of the gasification reactor below the distributor plate. The steam is generated in a series of three furnaces, which are shown in the lower left-hand portion of Figure 2 and are located within the high-pressure area. The steam supply tubing has been insulated to prevent heat losses. Strip heaters are also utilized in order to ensure that superheated steam is fed to the reactor under closely controlled conditions.

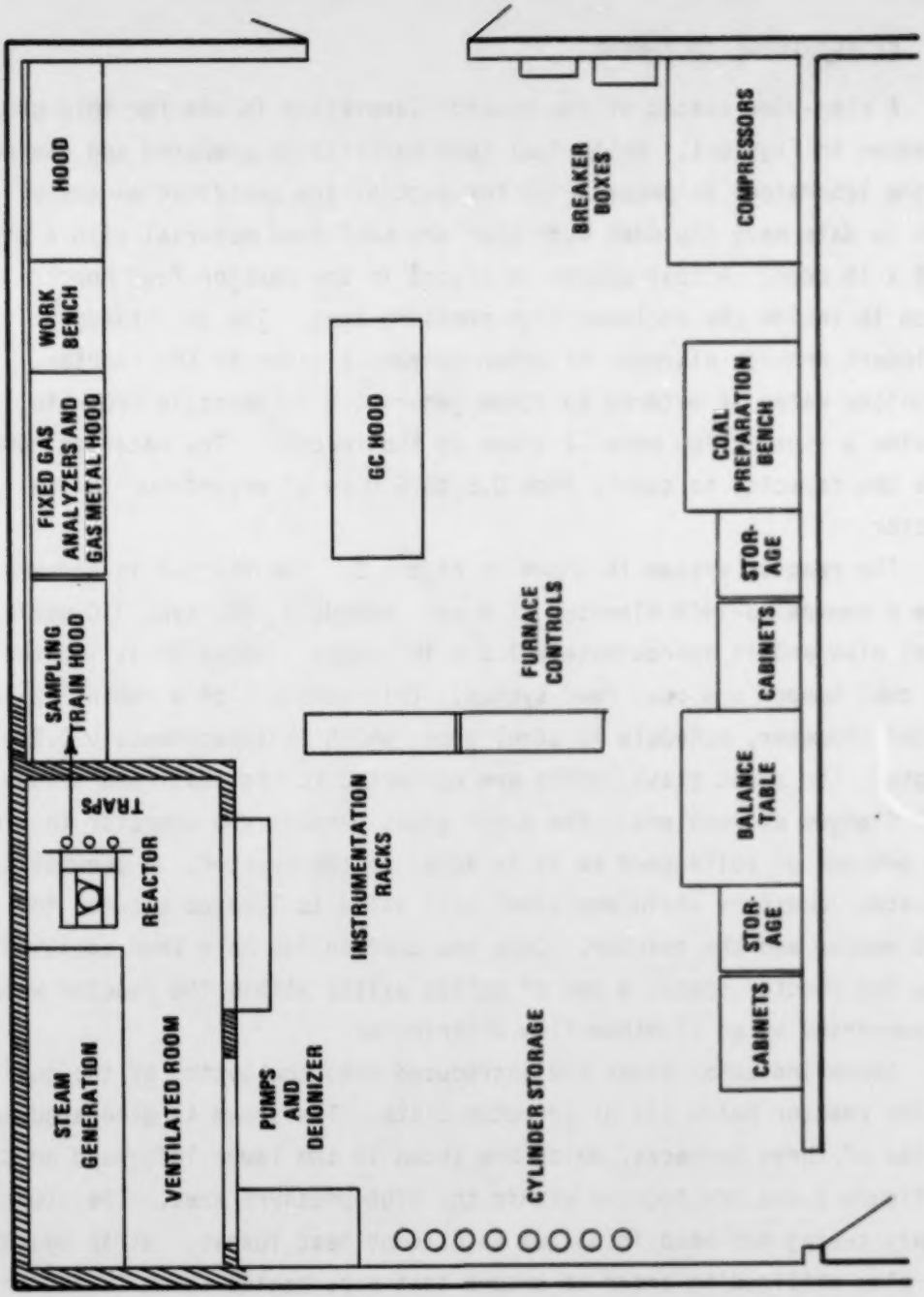
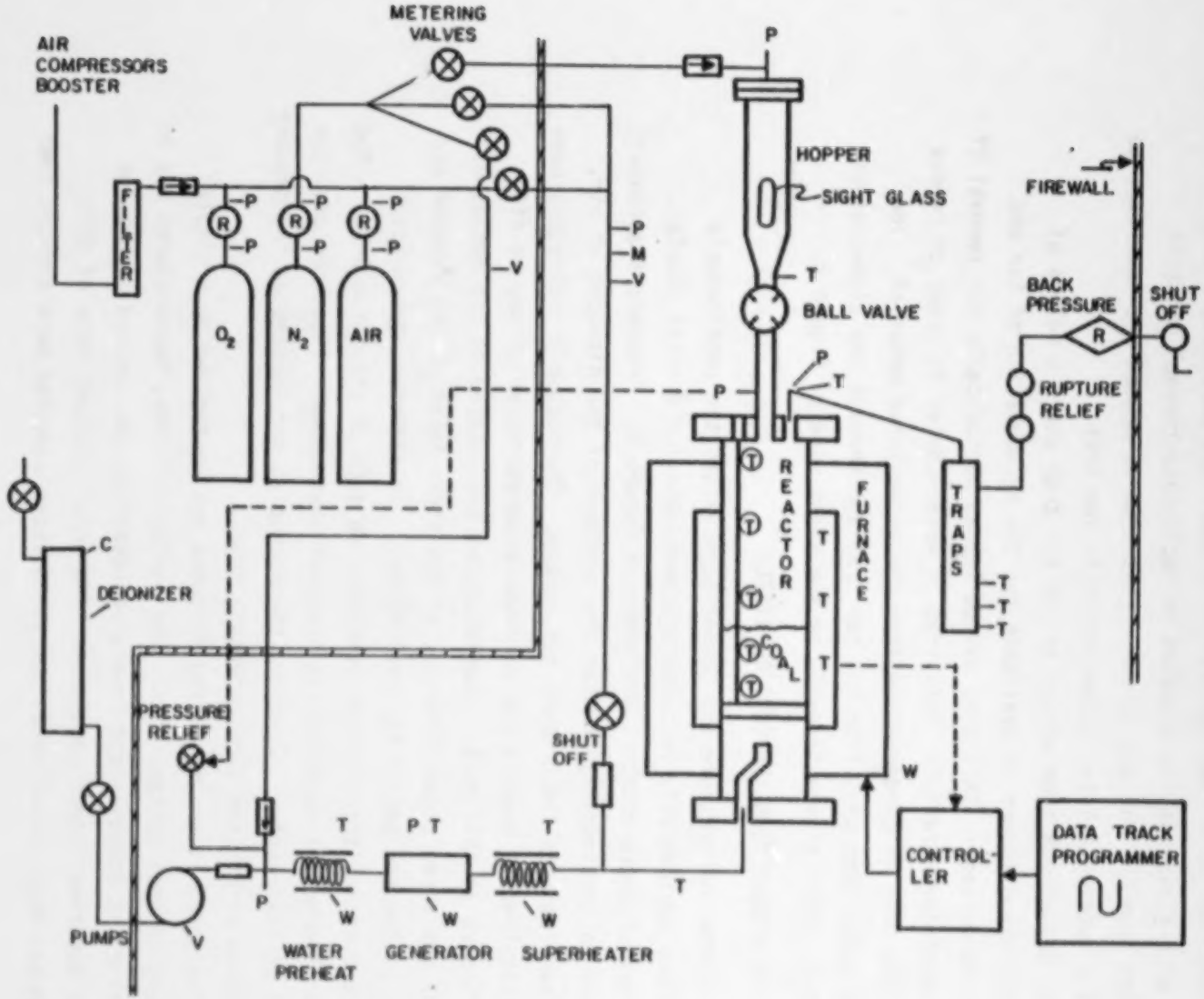


Figure 1. Plan-view sketch of laboratory.



C = CONCENTRATION
M = MASS FLOW
P = PRESSURE
R = REGULATOR
T = TEMPERATURE
V = VOLUME FLOW
W = WATTS

Figure 2. Gasification system.

The product gases that emerge from the reactor immediately enter the particulate trap. This trap contains a stainless steel braided cup which functions as a flow impinger. Further, the particulate trap is packed with glass wool as a medium to facilitate removal of solid particles from the hot gas stream. This trap is heated and insulated to prevent a substantial tar accumulation in the trap.

The gas stream then passes to the tar trap where a volume of approximately 8 liters is available for the accumulation of tar and aqueous condensate. This trap may be tapped periodically for removal of the accumulated material. This trap is water-cooled in order to remove the latent heat of condensation from the accumulated material. The product gases then pass from the tar trap and through the high-pressure enclosure, shown at the firewall on the right side of Figure 2.

3.2 DATA ACQUISITION AND CONTROL SYSTEM

A number of pressure and temperature values are continuously monitored, periodically recorded and available for digital display. Locations of these monitors are shown in Figure 2. Pressure transducers are used to continuously monitor the pressure of the nitrogen or air, the steam feed and the product gas stream. Thermocouple indicators have been installed to measure the various temperatures which may be of significance in this work. Thermocouples are located at the outlet of each of the three steam furnaces, at the steam inlet to the reactor and in the bottom and top of the coal hopper. In addition, the reactor furnace contains thermocouple detectors in each of its three zones. The reactor thermowell contains six distinct thermocouple locations over the length of the reactor. Further, thermocouples are located at the product gas outlet within the tar-condensate trap.

The three steam generating furnaces are controlled by a single Lindberg control system. Over long periods of time, temperatures may be controlled at steady-state levels representing the desired saturation and/or superheat steam condition. The on/off control mode of this system has made operation at low steam rates somewhat more erratic than

desired. This problem has been brought under control by the addition of insulation to the system and the use of strip heaters on the inlet steam line.

The vertical furnace that surrounds most of the reactor during operation is controlled in essentially the same manner as the three steam generating furnaces. This furnace does, however, contain three independently operated heated zones, each of which can demand a maximum of 2.6 kW. The furnace controller allows the selection of temperatures in the range of 200 to 1200°C for each zone. The three-zone electric furnace controller contains a datatrack programmer which will permit the introduction of any preselected temperature sequence for the three zones.

The measurement and control points for the gasification system are also shown in Figure 2. A Beckman continuous oxygen analyzer is used to monitor the oxygen level in the inlet gas flow or the product offgas stream when such is deemed desirable. The monitoring of the oxygen level can be regarded as a safety precaution as well. The presence of oxygen in an otherwise reducing gas system represents a potential combustion excursion or an explosive condition.

A backpressure regulator is used to maintain the gasification reactor pressure. By sensing fluctuations in the upstream pressure and varying the flow accordingly, the backpressure regulator is capable of maintaining the upstream pressure within ± 1 psi when operating at 1000 psi, i.e., ± 0.007 MPa at 7.0 MPa. After passing through the backpressure regulator, the gas stream flows through the wall of the high pressure area to the gas sampling system.

Pressure, temperature, and flow rate signals from the reactor control system are provided to the signal processor for collection, reduction, analysis, storage and reporting. The data acquisition system includes a signal processor (DEC PDP-11/34) with 64K words of memory, dual disk drive, an alpha-numeric CRT and a 30 cps DECwriter. (This signal processor and its accessories are being programmed for data processing in support of the gas chromatographic units which are used to analyze gaseous effluent samples.)

The CRT terminal and the hard copy printer (DECwriter) have a full keyboard, which permits dialog between the system and its users. These terminals are used for entry of operator's commands, display of process conditions and the generation of messages and data lists.

4.0 SAMPLING SYSTEMS

4.1 EQUIPMENT ITEMS

A versatile sampling system has been designed, assembled and interfaced with the coal gasification reactor. This system is intended to remove particulate solids, tars, aqueous condensates and other semi-volatile organic material, volatile organic compounds and fixed gases. Figure 3 shows the sampling train in relation to the coal gasifier.[17]

A particulate filter, which was described in the previous section, is intended to operate at or near the gas exit temperatures so as to remove only those solid particles which are entrained in the gas stream. During the preliminary runs, low volatile materials (tars) have been collected along with aqueous condensate in the water-cooled tar trap which follows the particulate trap. The tar trap is equipped with a valve at the bottom so that samples may be collected periodically during a reactor run. The traps have Varian high-vacuum flanges to ensure that gas releases do not occur. These traps are maintained at the system pressure, which was 1.2 MPa during the preliminary runs.

The gaseous effluent stream leaving the tar trap expands to nearly ambient pressure through the backpressure regulator. It enters the sampling manifold which is housed inside a fume hood maintained at or below 50°C. A three-way valve allows flow diversion to an XAD-2 cartridge during the surge period accompanying initial introduction of a coal sample into the reactor. Check valves are located downstream of the XAD-2 cartridges to facilitate proper gas routing. These cartridges are also maintained at or below 50°C by means of water circulation in their outer jackets. Tenax cartridges are located so that they may be used to sample the gas stream both before and after the XAD-2 cartridges. The total volume of gas pulled through the cartridges is kept within the limits of the breakthrough volume, which has been predetermined for the amount of Tenax resin employed.

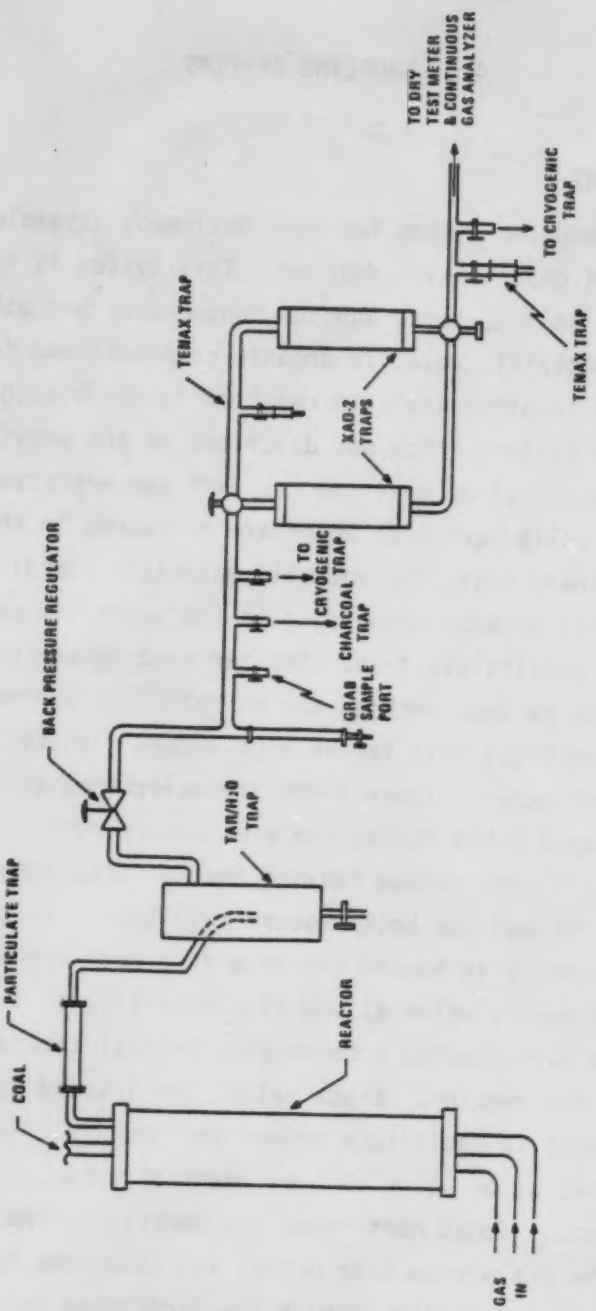


Figure 3. Gasifier and sampling train.

Tenax-GC resin is a porous polymer material that is based on 2,6-diphenyl-p-phenylene oxide. It was developed by AKZO Research Laboratories and is marketed by Enka, NV of the Netherlands.

The Amberlite XAD-2, a product of the Rohm and Haas Corporation, is a polystyrene-divinyl-benzene copolymer and has a crosslinked open lattice structure with a porosity between 0.4 and 0.5. This material, when prepared in the 20- to 50-mesh size used in this study, has a surface area of approximately 300 cm^2/gm. The Tenax cartridges have provided valuable information in the preliminary tests. The results from the use of Tenax cartridges have validated the efficacy of the XAD-2 cartridges for adsorbing organic compounds having a range of volatility values.

The total gas flow through the sampling system is measured downstream of the sampling devices by means of a Rockwell dry test meter. Gas volumes that have passed through the adsorbent trap are either monitored for their volumetric flow rate or redirected to the dry test meter so as to provide an accumulated total volume of gases generated by the gasification reactor.

Grab sample ports are used to collect individual sample volumes that are analyzed for permanent gases, sulfur-containing gases and C_1-C_6 hydrocarbons via gas chromatograph. The glass sample bulbs used for this sampling procedure are employed periodically for sample collection and then stored in a specially designed constant-temperature chest in order to preserve the samples until the end of the run, i.e., approximately four hours, for subsequent gas chromatographic analysis. The glass-to-metal fittings are ultratorr vacuum fittings, providing for leakproof operation from high vacuum to 0.30 MPa (25 psig). All metal fittings are of stainless steel and are of the flangeless, ferruled type.

4.2 SAMPLING PROCEDURES

At the conclusion of each run, the particulate trap is removed from the system. The collected materials are removed from the trap by a methylene chloride wash sequence. The wash solution is filtered to

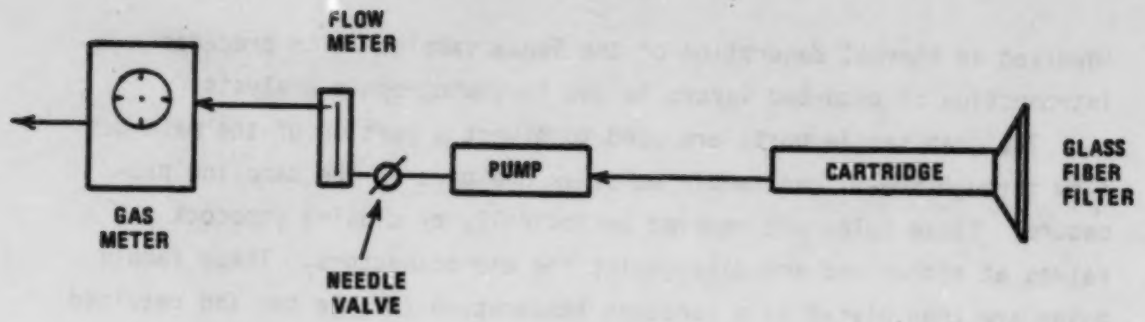
determine the residue of insoluble material. The solution and residue are retained for analysis.

The contents of the tar trap are removed periodically during the reactor operation. These samples consist of tar materials and aqueous condensates. The samples are marked, weighed and delivered to the analytical chemical laboratory for analysis.

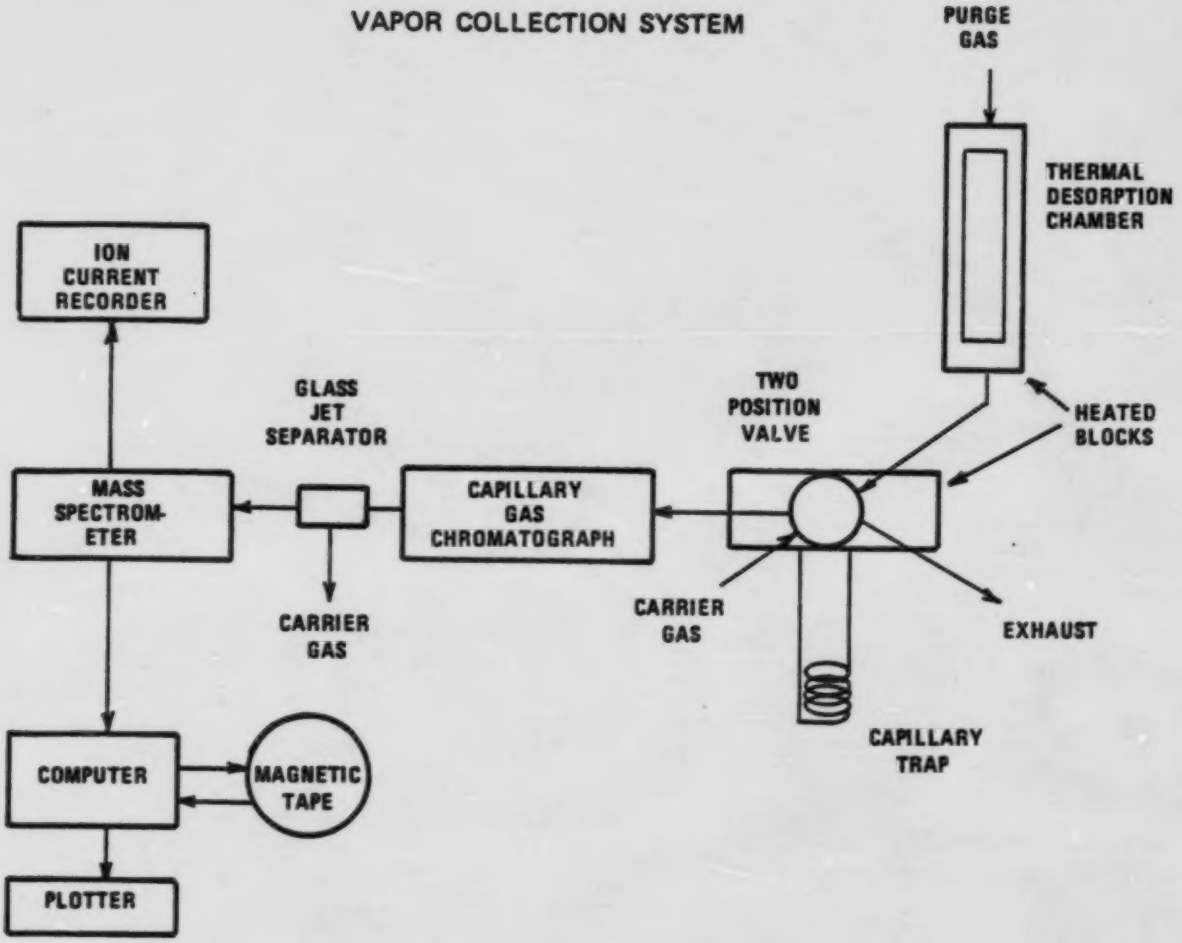
The sampling strategy for the collection of individual glass bulb samples, as well as the Tenax and XAD-2 samples, is planned before each run is conducted. This includes planning the time intervals between various bulb samples, the times for collection of the individual Tenax cartridge samples and the time at which the switchover will be made from the surge XAD-2 to the steady-state XAD-2 cartridge sample. A run is initiated with nitrogen flow passing to the surge XAD-2 cartridge and with continuous purging of the first sampling bulb with nitrogen.

Typically the surge XAD-2 sample is taken during the first 40 minutes of the run at which point the valving is used to switch the stream flow to the steady-state XAD-2 cartridge. The XAD-2 resins in both the surge and the steady-state cartridges are contained within a cylindrical packed section which is 64 mm in diameter and 330 mm in length. When feasible, six additional XAD-2 samples are obtained utilizing the grab sample ports of the sampling system. Three liters/min of product gas are passed for five minutes through each of these cartridges, for example.

The Tenax samples are obtained about two hours after the start of each run. The Tenax resin is contained within the cylindrical packed section, 12 mm in diameter, 65 mm in length; some 200 ml of gas is passed through the Tenax cartridges in 30 secs. The upstream Tenax cartridge is utilized on the gas stream prior to its passsage through the steady-state XAD-2 cartridge. The downstream Tenax cartridge is utilized for sampling the gas stream downstream of the steady-state XAD-2 cartridge. A diagram of the sampling technique for Tenax cartridges is displayed in Figure 4. This figure also indicates the equipment



VAPOR COLLECTION SYSTEM



ANALYTICAL SYSTEM

Figure 4. Vapor collection and analytical systems for organic vapors.

involved in thermal desorption of the Tenax samples which precedes introduction of desorbed vapors to gas chromatographic analysis.

The grab sample ports are used to divert a portion of the main gas flow through 500-ml gas sample bulbs as one part of the sampling procedure. These bulbs are removed periodically by closing stopcock valves at either end and disengaging the end connectors. These sample bulbs are then placed in a constant temperature storage box and retained until the end of the run at which time they are analyzed using a gas chromatograph.

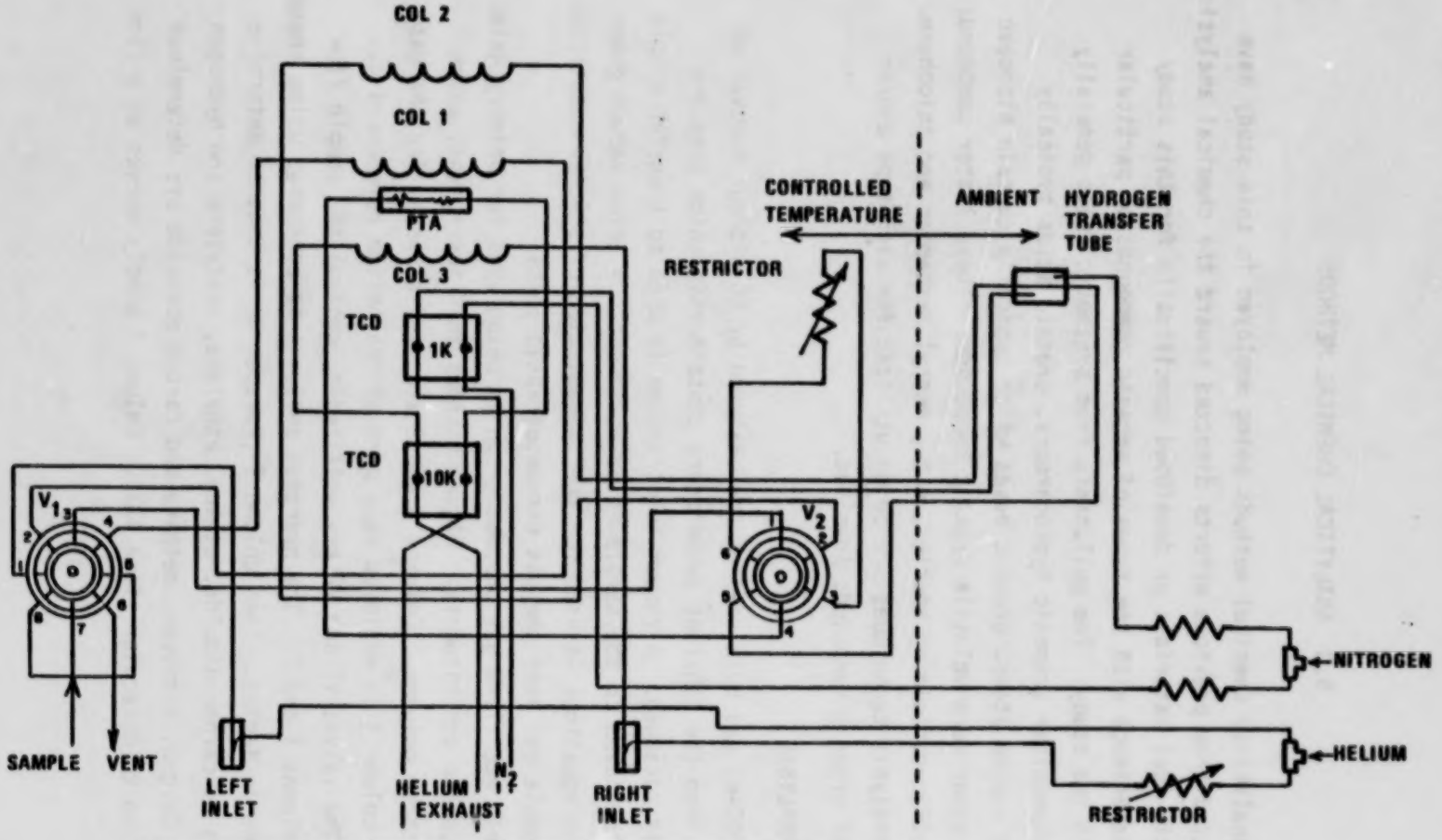
5.0 ANALYTICAL CHEMICAL METHODS

The analytical chemical methods being employed in this study have been selected from previous efforts directed toward the chemical analysis of synthetic fuel materials or developed specifically for this study based on experience with the types of organic compounds of particular interest to the study. The pollutants from synthetic fuels generally include polynuclear aromatic hydrocarbons, organic acids typically containing oxygen atoms, organic bases which typically contain nitrogen atoms and other more volatile organic compounds. These latter compounds include sulfur-containing species, e.g., methyl mercaptan and thiophene. Specific analysis techniques are being utilized for each type and/or category of organic compounds involved.

5.1 GAS ANALYSIS

The 500-ml gas bulb samples are analyzed by GC without removal of the bulbs from the constant temperature container in which they are temporarily retained. A vacuum inlet system is used to transfer sample gas from the bulbs to the sample inlet equipment. A Heise vacuum gauge with 1-ml graduations is used for the introduction of precise quantities of this sample gas into the gas chromatographic units.

A Carle AGC 111-H gas chromatograph is being used for primary gases and hydrocarbon constituents. Figure 5 shows this instrument, which contains three columns. Columns 1 and 2 are used directly for the gas analysis; column 3 is employed as a part of the helium referenced gas system. The valves V1 and V2 are utilized to control the sample flow through columns 1 and 2. The hydrogen analysis is conducted using these two columns in series. Then column 1 (Porapak N) is used to determine the levels of carbon dioxide, ethane, ethylene, acetylene and hydrogen sulfide. Oxygen, nitrogen, methane and carbon monoxide are determined using column 2 (molecular sieve 13X). Column 3 simply serves as a flow



COL 1	6' - 60/80 PORAPAK N
COL 2	7' - 80/100 MOLECULAR SIEVE 13X
COL 3	6' - 8% OV-101 ON 80/100 CHROMOSORB W AWDMCS

Figure 5. Schematic of gas chromatograph.

restrictor for the reference side of the thermal conductivity cell that is used with this gas chromatograph.

The vacuum inlet system is also utilized for the introduction of sample bulb gases to a Perkin-Elmer 3920B gas chromatograph. This instrument is equipped with a thermal conductivity (TC), flame ionization detector (FID) and a flame photometric detector (FPD) for the analysis of C_1-C_6 hydrocarbons as well as sulfur-containing gases. A Durapak phenyl isocyanate column in combination with the TC or FID is used for the analysis of the hydrocarbon gases. The sulfur-containing gases, H_2S, COS, CS_2, mercaptans and thiophene are being successfully analyzed using a Carbopak B/1.5% XE60/1% H_3PO_4 column and the FPD. Calibration gases have been obtained from the National Bureau of Standards and Scott Environmental Technology, Inc. The FPD is known to have a six-fold linear dynamic range and only relative standards are needed for its calibration. The nonlinearity of the FPD has been overcome by transforming the analog signal obtained from it to a logarithmic one. Accurate calibration has been performed using compounds of interest at varying concentrations.

5.2 VOLATILES ANALYSIS

As was seen in Figure 4, Tenax cartridges are placed into a desorption chamber and heated to desorb the volatile organic compounds that are collected in the sampling system. A purge gas transports these volatiles to a capillary trap where they are condensed for subsequent analysis. The inlet manifolds for introducing the sample into the analytical instrument consists of four main components:

1. Desorption chamber.
2. Two-position high pressure (low volume) valve.
3. Gold-plated capillary trap.
4. Temperature controller.

The adsorbed organic material on a sample of Tenax resin is vaporized by rapid heating to 175°C. The vapor is transferred into a high resolution

capillary GC column. This column is interfaced to a double-focusing mass spectrometer (Varian CH7). During the analysis of each sample, the mass spectrometer repeatedly scans the column effluent approximately every 7 seconds. The scans range from 28 to 400 atomic mass units. The information from these scans is accumulated by an on-line computer onto a magnetic tape. The data include peak intensities, total ion current (TIC) values and Hall probe signals (instrument calibration indicators).

XAD-2 samples are prepared for analysis by removing a 20-gram portion of the resin sample which contains adsorbed material. Extraction with methylene chloride follows for up to 24 hours. The extract is then concentrated by evaporation under reduced pressure. The final volume of extract is 1-ml.

The volatile organic samples thus obtained from the Tenax and XAD-2 cartridges are utilized in a combined gas/liquid chromatography column/mass spectrometer/computer. Further details on this analytical chemical technique are presented by Sparacino[28,29] and Pellizzari.[22]

The processing of mass spectrometer data involves extraction of the TIC data and the preparation of a plot of TIC vs. the spectral number. A computer then generates mass spectral plots of the compound(s) represented by individual peaks on the TIC plots. Mass spectral plots display ion mass vs. ion intensity and represent the characteristic mass spectra of the compound(s). The components of the sample are then identified by comparing the mass cracking pattern of the unknown mass spectra to an eight-major peak index of mass spectra. The identification can be confirmed by comparing the cracking pattern and elution temperature on two different GC columns with authenticated compounds. This technique has been used by Pellizzari, et al.[23] to identify some 200 components in coal gasification samples. Successful identification has been achieved with approximately 200 ng of individual components transferred onto the capillary column.

5.3 SEMIVOLATILES ANALYSIS

The semivolatile materials, sometimes called nonvolatile materials, represent the organic material collected in the tar/water condensate

trap. This is an exceedingly complex sample for which a complete analysis methodology has not been fully developed. The methodology used herein involves extraction with methylene chloride followed by GLC/MS/computer analysis. The methylene chloride extracts organic material from the aqueous phase. This extract is then concentrated and subjected to chemical analysis. A sample is provided to the inlet system of a high resolution glass capillary chromatography column which functions on the inlet system of a gas chromatograph. The chromatography column was specifically prepared in the laboratory at RTI for use in these studies. With it, severe tailing of phenol-type compounds, characteristic of commercially available columns, has been avoided.

The tar fraction from the tar trap is partitioned using a technique modified from that of Novotny, et al.[20] The partitioning scheme is depicted in Figure 6. The tars are thus partitioned into six fractions, namely, acidic compounds, basic compounds, nonpolar neutral, polar neutrals, PNA and insoluble materials. The procedure has been validated through the testing of standard mixtures and by the use of radionuclide-labelled materials.

The acid, base and PNA fractions are analyzed using gas chromatography/mass spectrometer/computer analysis techniques. The use of peak areas from the GC trace is not feasible due to the complexity of the sample. The two mass spectrometers which have been used for this purpose are a Finnigan 3300 and LKB 2091. Compound identification is performed as described above in Section 5.2.

Quantitation of specific compounds has also been performed for some selected samples. The quantitation process involves monitoring specific ions and comparing their ion intensities with those of carefully chosen internal standards. Primary standard samples are prepared containing known quantities of primary standard compounds. In addition, internal standard compounds are added to both primary standard samples and the unknown samples. The internal standards that have been used include pentadeutero-phenol, heptadeutero-quinoline and decadeutero-anthracene. These compounds represent acidic, basic and PNA materials, respectively.

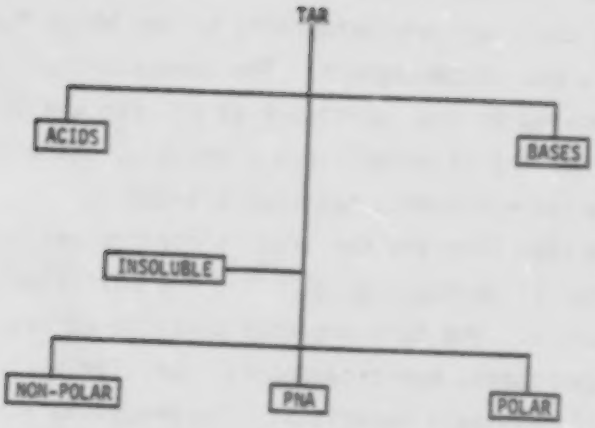


Figure 6. Solvent partition scheme for tars.

The primary standard samples are analyzed to generate relative molar response values for the specific ions resulting from the primary standard compounds. Quantitation is then achieved by using three pieces of information: quantity of internal standards added to each unknown sample; the measured peak area obtained for the primary ion of the internal standards; and the measured peak area for the selected ion of each unknown sample. This technique has recently been validated for both the quadrupole and the magnetic sector mass spectrometer instruments used in this work. Both instruments have employed high resolution glass capillary chromatography columns containing OV-101 or SE-30 stationary phases. Table 1 provides operating parameters which have been utilized with this system.

TABLE 1. OPERATING PARAMETERS FOR GLC-MS COMP SYSTEM

Parameter	Setting
Inlet-manifold	
desorption chamber	260°C
valve	180°C
capillary trap - minimum	-195°C
maximum	+175°C
thermal desorption time	10 min.
GLC - (Gas/Liquid Chromatograph)	
SCOT capillary columns	20°C, 4 C°/min.
carrier (He) flow	~3 ml/min.
transfer line to ms	210°C
MS - (Mass Spectrometer)	
scan range	m/e 20 → 300
scan rate, automatic-cyclic	1 sec/decade
filament current	300 μA
multiplier	6.0
ion source vacuum	~4×10^{-6} torr

6.0 EXPERIMENTAL RESULTS

The most significant experimental results obtained in this study to date deal with the reactor performance and the analysis of chemical substances generated by the reactor. Reactor performance testing has focused on coal gasification under carefully controlled (preselected) conditions for a sustained time period. The chemical analyses that have been obtained include data for the primary gas products, the volatile organic species, and the semivolatile organic materials which have been collected in the tar trap.

6.1 REACTOR PERFORMANCE

Reactor performance testing has involved the running of three or more test runs per month. Four runs have been selected from the initial 16 experimental test runs for description in this report. These runs, designated as numbers 2, 4, 6 and 16, are runs for which sufficiently complete information is available to provide a meaningful description and to allow comparisons. The other runs have been useful for overall system characterization and debugging purposes.

6.1.1 Overall Feed Conversion and Reactor Temperature Profiles

As seen in Tables 2 and 3, the initial runs were conducted utilizing a char that had previously been generated from Western Kentucky coal in the COED process.[18] The elemental and proximate analyses for the feed charge and the reactor residue subsequent to reaction are shown in Table 2. Data on the gasification tests are provided in Table 3. As was anticipated, the percentage of carbon conversion was a direct function of the total residence time; however, it was observed that the degree of sulfur conversion during the reactor test was substantially higher than that of the carbon conversion. This was found to be the case not only for the char material used in Runs 2 and 4 but also for the Illinois No.6 coal used in Runs 6 and 16. Generally, this reflects that the sulfur species

TABLE 2. COAL, CHAR AND RESIDUE ANALYSES

Quantity	FMC Char (Runs 1,2,3,4)	Residue (Run 1)	Residue (Run 2)	Residue (Run 3)	Residue (Run 4)	Raw Coal (Runs 5,6)	Residue (Run 5)	Residue (Run 6)
Carbon, %	74.02	13.82	69.81	52.16	55.72	63.26	68.54	57.78
Hydrogen, %	1.48	0.82	1.11	9.73	0.54	4.61	0.63	0.60
Oxygen, %	1.7	<0.1	1.0	---	0.43	7.37	0.59	1.35
Nitrogen, %	1.3	0.3	0.9	0.39	0.29	1.38	0.70	0.48
Sulfur, %	1.8	0.2	1.0	1.16	0.31	3.01	1.08	0.51
Ash, %	19.7	85.0	26.2	43.9	42.0	13.52	26.41	34.64
Moisture, %	1.0	0.9	1.5	2.38	0.70	6.85	2.05	4.64
Volatile Matter, %	7.8	6.3	4.3	2.83	2.17	32.58	3.87	2.13
Fixed Carbon, %	71.5	7.8	68.0	50.8	55.1	47.05	67.67	58.59
Higher Heating Value, Btu/lb	11,090	570	10,315	7,615	8,218	11,331	9,882	8,540
Free Swelling Index, FSI	<1.0	0.0	0.0	0.0	0.0	3.5	0.0	0.0

TABLE 3. DATA ON RTI PRELIMINARY GASIFICATION TESTS

Run No.	Average Maximum Temp. (°K)	Total Reactor Pressure (MPa)	Total Reaction Time (hr.)	Feed		Residue		Conversion	
				Amount (kg) / Heating Value (kcal/kg)	Carbon (%) / Sulfur (%)	Amount (kg) / Heating Value (kcal/kg)	Carbon (%) / Sulfur (%)	Carbon (%)	Sulfur (%)
2 FMC Char	1,018	1.5	1.45	0.175 6,302	74.8 1.82	0.118 5,817	70.9 1.01	36.1	62.6
4 FMC Char	1,054	1.5	4.63	0.597 6,302	74.8 1.82	0.303 4,597	56.11 0.31	58.0	93.8
6 Illinois No.6 Coal	1,079	1.5	4.50	1.034 6,757	67.9 3.23	0.372 4,975	60.6 0.53	67.9	94.1
16 Illinois No.6 Coal	1,208	1.5	4.28	1.494 6,536	65.0 2.85	0.325 2,160	35.9 1.06	88.6	92.3

present are more volatile and more reactive than some of the carbonaceous materials present. This is not surprising in that the conditions of reaction which were imposed are those for pyrolysis and partial gasification (the carbon/steam reaction).

Tables 4, 5 and 6 present sample analysis information on the primary gas stream generated by the reactor. These data are also displayed graphically in Figures 7 through 9. It is seen in Figure 7, which represents a char material gasified in Run 4, that the methane level experiences only a small variation over the entire duration of the run. This is to be contrasted with the behavior shown in Figures 8 and 9, which represents the gasification of Illinois No.6 coal, in which the methane content displays its largest value quite early in the reaction process. This indicates that methane is being produced primarily by the pyrolytic decomposition of volatile matter from the coal. Alternatively, the hydrogen content of the product gas was found to increase to a relatively high value on a nitrogen-free basis and retained an essentially constant value over the remainder of the run. The carbon monoxide and carbon dioxide levels of product gas were found to increase over the initial transient period to essentially steady values intermediate to those for the methane and hydrogen.

The test runs that have been performed using the RTI laboratory coal gasification reactor can be divided into two general categories: external heat tests and combustion heat tests. In the case of external heat test runs, the reactor is operated without air (or oxygen) supplied to the inlet. The thermal energy required to maintain the reactor at the desired operating temperature for external heat tests is supplied by the vertical furnace which surrounds the reactor. Those runs for which air represents one of the inlet flow streams are referred to as combustion heat tests since a certain amount of thermal energy for maintaining the bed temperature results from the partial combustion reactions which occur within the bed. For these runs, the external vertical furnace may also be used to provide additional thermal energy required to achieve a predetermined operating temperature level.

TABLE 4. SAMPLE ANALYSES FOR GASIFICATION RUN 4
(Char dropped after 23 minutes from blank sample collection)

On Stream → Time From System Blank (Minutes)		0	62	123	183	204	264
Gas	Unit						
N_2	%	>98	74.5	27.7	8.8	6.7	14.5
H_2	%	<0.01	11	38.8	46.7	48.0	43.3
CO	%	<0.01	0.9	3.1	10.8	15.9	18.4
CO_2	%	0.02	8.6	20.0	22.5	20.8	14.8
CH_4	%	0.08	4.9	8.9	9.6	10.2	7.0
C_2H_4	ppm	<11	16	47	8.6	6.8	2.1
C_2H_6	ppm	<1	160	380	48	32	12
H_2S	%	<0.01	0.58	0.61	0.62	0.59	0.11
COS	ppm	0	8.4	10.5	147	95	69.3

Gasifier Conditions

Initial char weight: 600 grams
Nitrogen Flow: 500 mℓ/minute (STP)
Steam Flow: 8 gms/minute
Temperature: Programmed profile: Ramp increase 700-950°C, ramp decrease 950-775°C.
Pressure: 1.5 MPa (200 psig)

TABLE 5. SAMPLE ANALYSES FOR GASIFICATION RUN 6

On Stream Time (Min) →		5	18	45	73	112	139	152	227
Gases	Unit								
H_2	%	2.69	8.62	16.18	28.55	46.81	49.32	51.35	50.11
CO_2	%	1.47	3.34	5.62	9.83	17.88	19.3	18.68	20.09
CO	%	1.49	2.76	2.87	3.93	6.96	12.75	16.96	17.34
CH_4	%	6.56	15.42	25.36	17.69	7.59	4.62	3.78	2.96
C_2H_6	ppm	11100	25100	38500	4800	270	92	63	22
C_2H_4	ppm	2900	5000	8300	1000	96	31	22	8
C_3H_6	ppm	2800	5600	8800	1000	52	26	20	7
C_3H_8	ppm	3300	7900	9600	1100	120	23	17	5
H_2S	ppm	13600	29400	34500	12000	5900	6500	5300	5100
COS	ppm	53	100	45	83	44	66	48	24
CH_3SH	ppm	51	45	100	34	10	10	3	3
Thiophene	ppm	68	151	184	96	< 5	< 5	< 5	< 5

Gasifier Conditions:
Illinois No.6 Coal Weight: 1034 gms.
Nitrogen Flow: 1 liter/min (STP)
Steam Flow: 20.7 gms/min.
Temperature: Programmed Profile: Ramp increase 600-925°C.
Pressure: 1.5 MPa (200 psig).

TABLE 6. SAMPLE ANALYSES FOR GASIFICATION RUN 16

On Steam Time (Min) →										
Gases	Unit	9	20	30	43	60	78	90	105	120
H_2	%	23.46	32.56	39.60	37.74	37.28	36.58	35.98	35.82	34.30
CO_2	%	4.17	4.99	8.53	11.01	15.79	16.87	17.14	17.42	17.54
CO	%	6.78	8.61	13.43	14.48	17.15	16.98	16.37	16.22	15.65
CH_4	%	28.40	22.73	6.66	2.98	2.57	2.47	2.42	2.43	2.38
C_2H_6	ppm	13,345	8,736	1,465	153	48	37	28	25	29
C_2H_4	ppm	11,005	4,836	660	56	10	8	5	4	6
C_3H_6	ppm	1,894	1,036	154	16	1	----	----	----	----
C_3H_8	ppm	1,525	780	136	15	1.3	----	----	----	----
H_2S	ppm	18,986	18,667	7,278	5,129	5,068	4,072	3,979	4,024	3,947
COS	ppm	48	45	33	29	32	33	30	27	33
CH_3SH	ppm	27	9	<5	----	----	----	----	----	----
Thiophene	ppm	858	576	48	28	6	<5	----	----	----

Gasifier Conditions:

Illinois No. 6 Coal Weight: 1573 gms.
Nitrogen Flow: 5 liter/min (STP)
Steam Flow: 13.7 gms/min
Temperature: Programmed Profile: Ramp increase 255-973°C.
Pressure: 1.5 MPa (200 psig).

(continued)

TABLE 6. SAMPLE ANALYSES FOR GASIFICATION RUN 16 (continued)

On Steam Time (Min) →											
Gases ↓	Unit	135	151	165	180	195	210	225	240	255	270
H_2	%	35.07	33.87	34.29	33.38	33.45	32.35	31.43	29.45	29.76	27.62
CO_2	%	18.15	18.05	18.48	18.80	18.72	18.66	18.70	19.08	19.24	19.20
CO	%	15.06	14.53	14.15	13.61	13.13	12.76	12.23	11.67	11.34	11.76
CH_4	%	2.36	2.29	2.32	2.28	2.22	2.14	2.03	1.93	1.85	1.66
C_2H_6	ppm	23	24	20	24	22	17	17	16	13	12
C_2H_4	ppm	4	6	3	5	5	3	4	3	3	3
C_3H_6	ppm	----	----	----	----	----	----	----	----	----	----
C_3H_8	ppm	----	----	----	----	----	----	----	----	----	----
H_2S	ppm	3,908	3,351	3,800	4,042	4,033	4,120	3,736	3,149	3,436	3,265
COS	ppm	27	26	27	26	27	25	25	24	23	22
CH_3SH	ppm	----	----	----	----	----	----	----	----	----	----
Thiophene	ppm	----	----	----	----	----	----	----	----	----	----

Gasifier Conditions:

Illinois No.6 Coal Weight: 1573 gms.
Nitrogen Flow: 5 liter/min (STP)
Steam Flow: 13.7 gms/min
Temperature: Programmed Profile: Ramp increase 255-973°C.
Pressure: 1.5 MPa (200 psig).

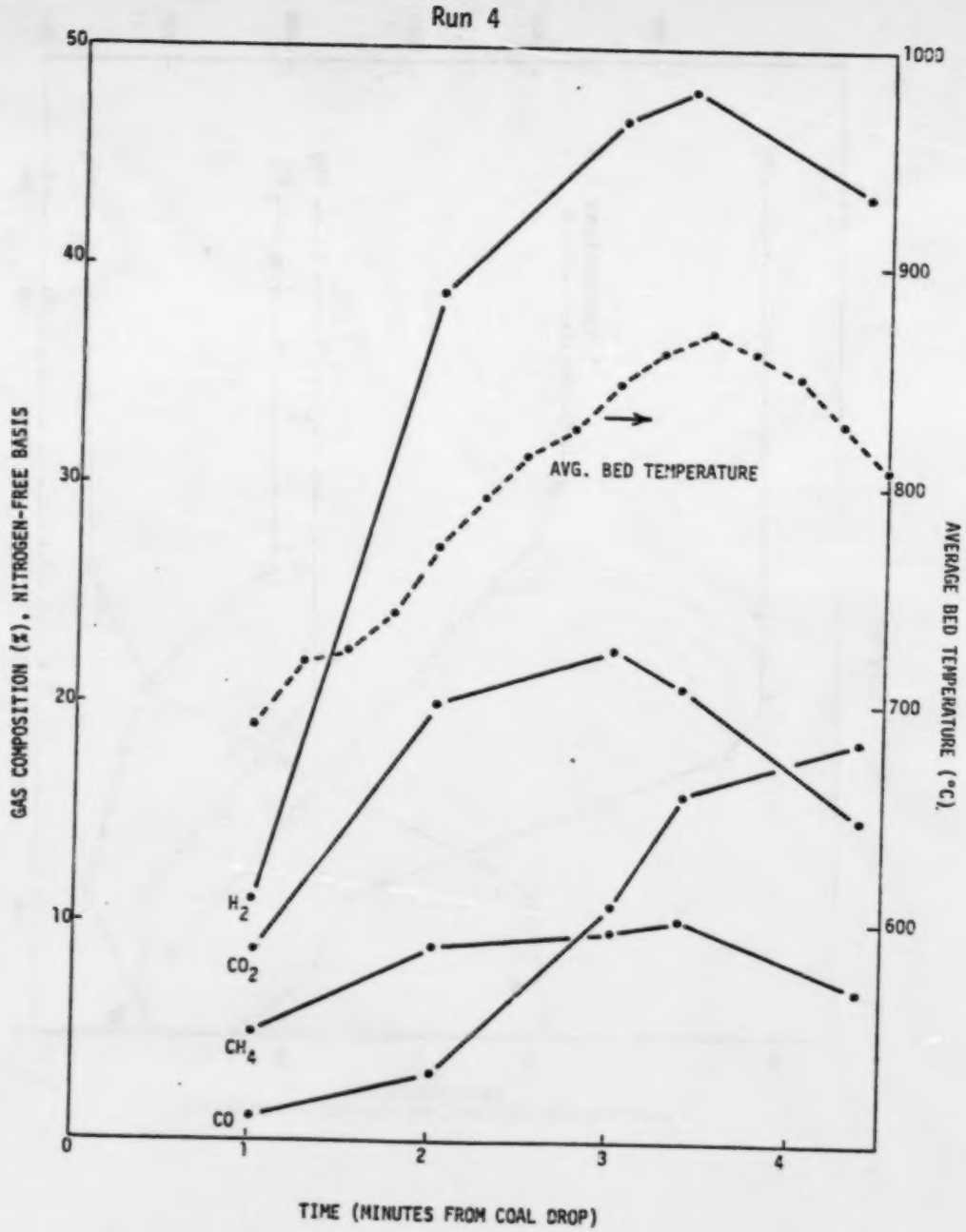


Figure 7. Major product gas concentrations (char run 4).

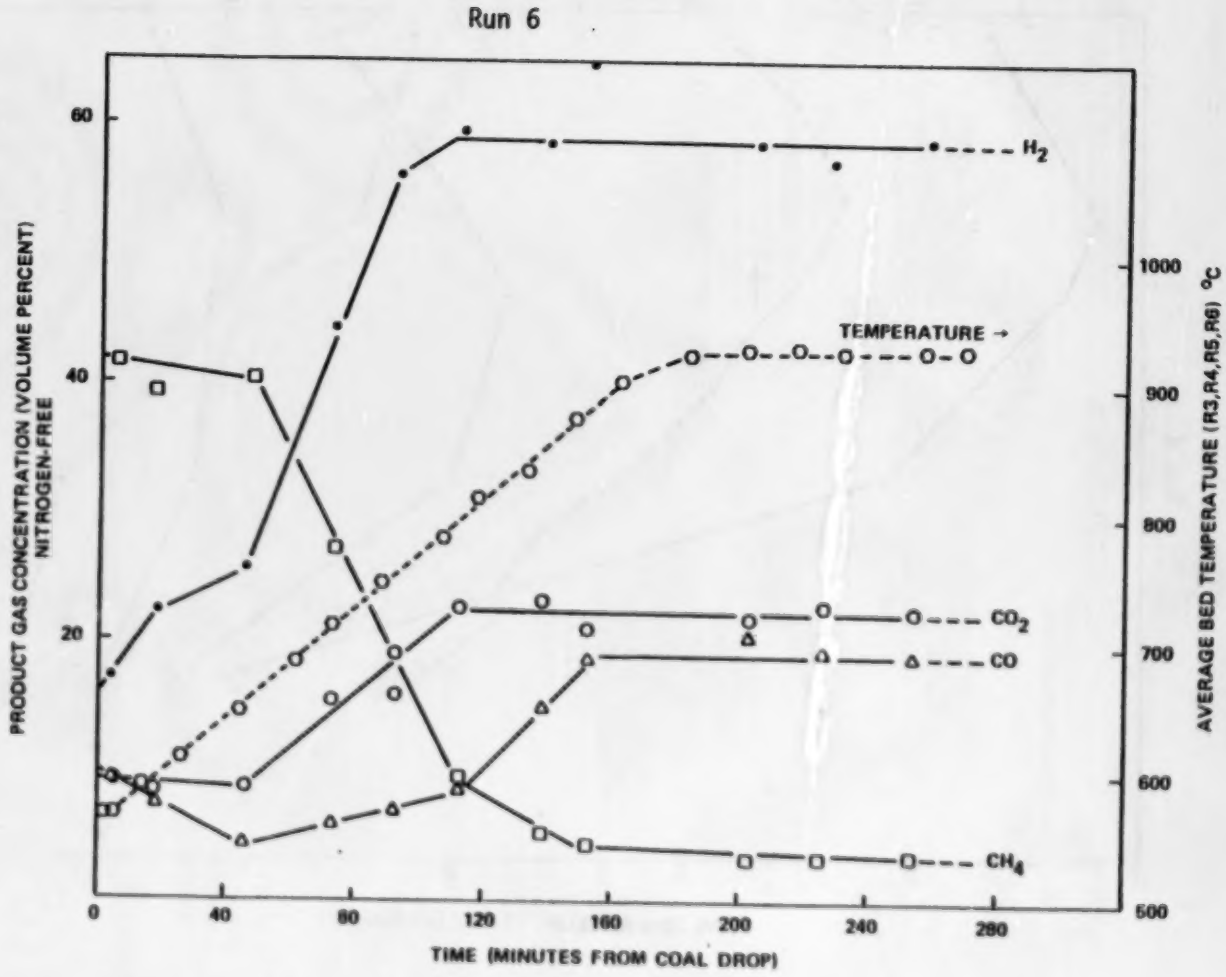


Figure 8. Major product gas concentrations (coal run 6).

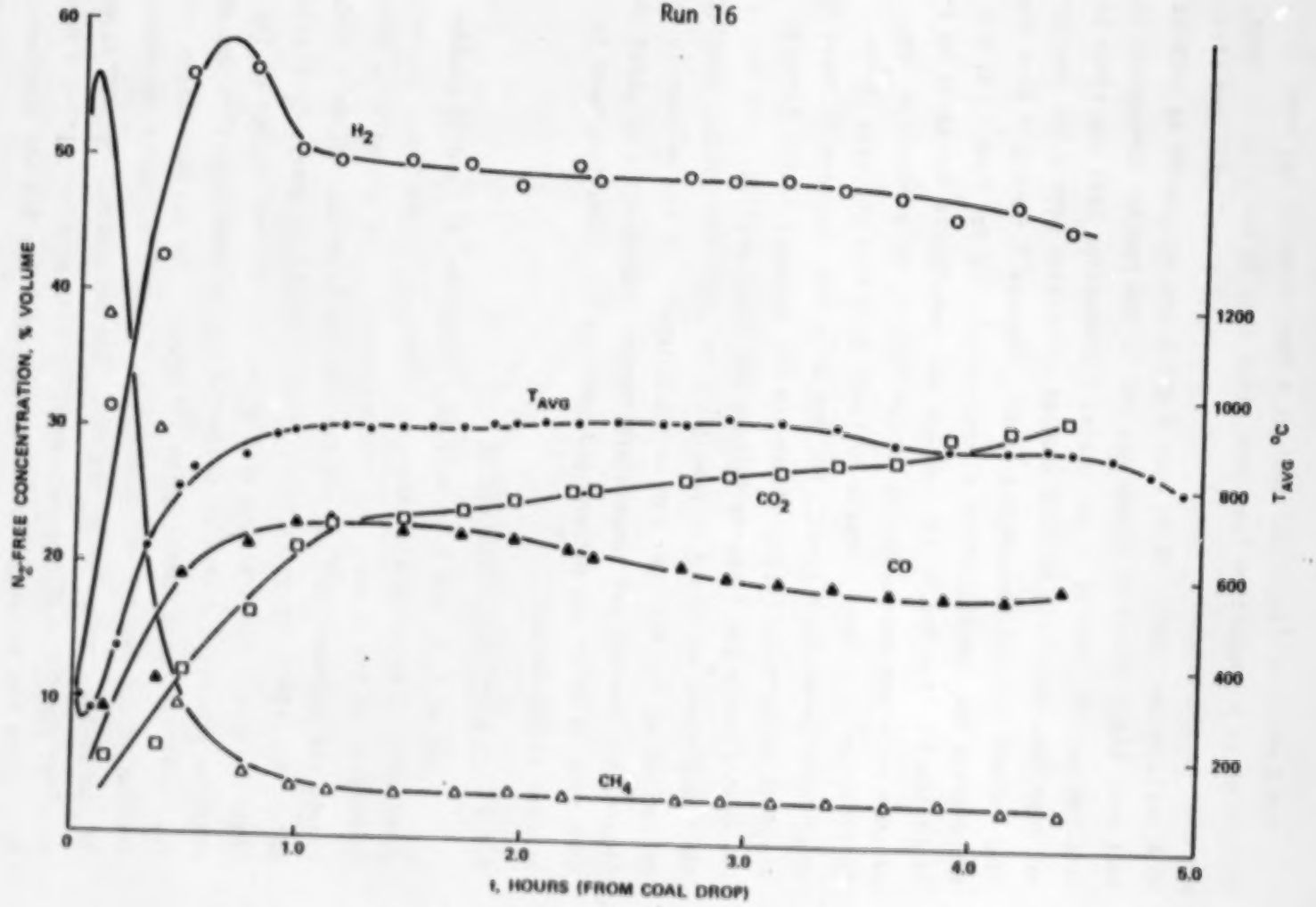


Figure 9. Major product gas concentrations (coal run 16).

Run 2 which utilized coal char as a feed material has been designated as a combustion heat test since air, in addition to steam, was used in the reactor. Runs 4 and 6 employed a coal char and Illinois No.6 coal, respectively. Both Runs 4 and 6 are designated as external heat runs since no air or oxygen was fed to the reactor throughout the test run period. Run 16 is designated a combustion heat run since air was supplied, resulting in some heat of combustion within the reactor to help support the bed temperature level. Figures 7 through 9 also display the average bed temperature as a function of time for Runs 4, 6, and 16, respectively. For Run 4, the average bed temperature increases to a maximum value and decreases, in linear fashion, as a result of the introduction of a ramp increase followed by a ramp decrease in the programmed temperature input. For Run 6, a ramp increase followed by a constant temperature is introduced via the external heater furnace. The response closely and linearly follows the input profile. For Run 16, the temperature was found to remain steady after the initial devolatilization period for the coal had been completed. As can be seen in this figure, the average bed temperature reaches steady-state at about the same time at which the methane and hydrogen concentrations seem to achieve steady values.

6.1.2 Low Level Gas Constituents

Tables 4, 5, and 6 as well as Figures 10, 11, and 12 (sulfur gases only) display data on the concentrations of the minor gaseous components of the primary gas product stream. The tables show that ethane and hydrogen sulfide are the two low level constituents that occur in largest concentrations. These components generally display their largest concentrations within the initial few minutes of the reaction process. A similar statement can be made regarding the other low level gas constituents which are shown. The maximum ethane concentration of 3.8 percent was observed in Run 6. This value decreased to 22 ppm at the conclusion of the run. The maximum H_2S concentration occurred for Run 6 at the same sampling time at a value of 3.5 percent. This value had decreased to 0.5 percent when the run was concluded. Measurable quantities of ethylene, propane, propylene, carbonyl sulfide,

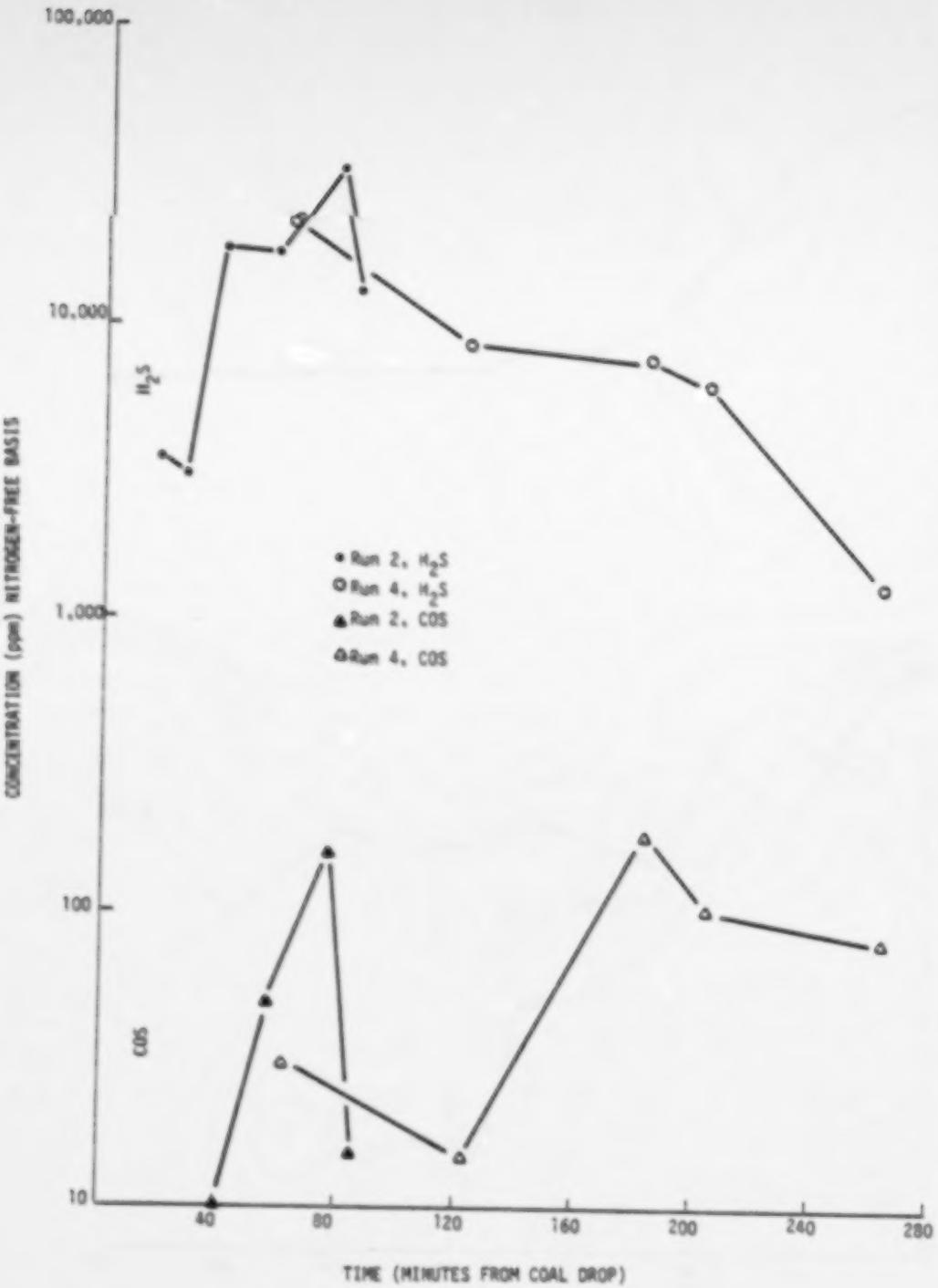


Figure 10. Sulfur-containing gas compositions (char runs 2 and 4).

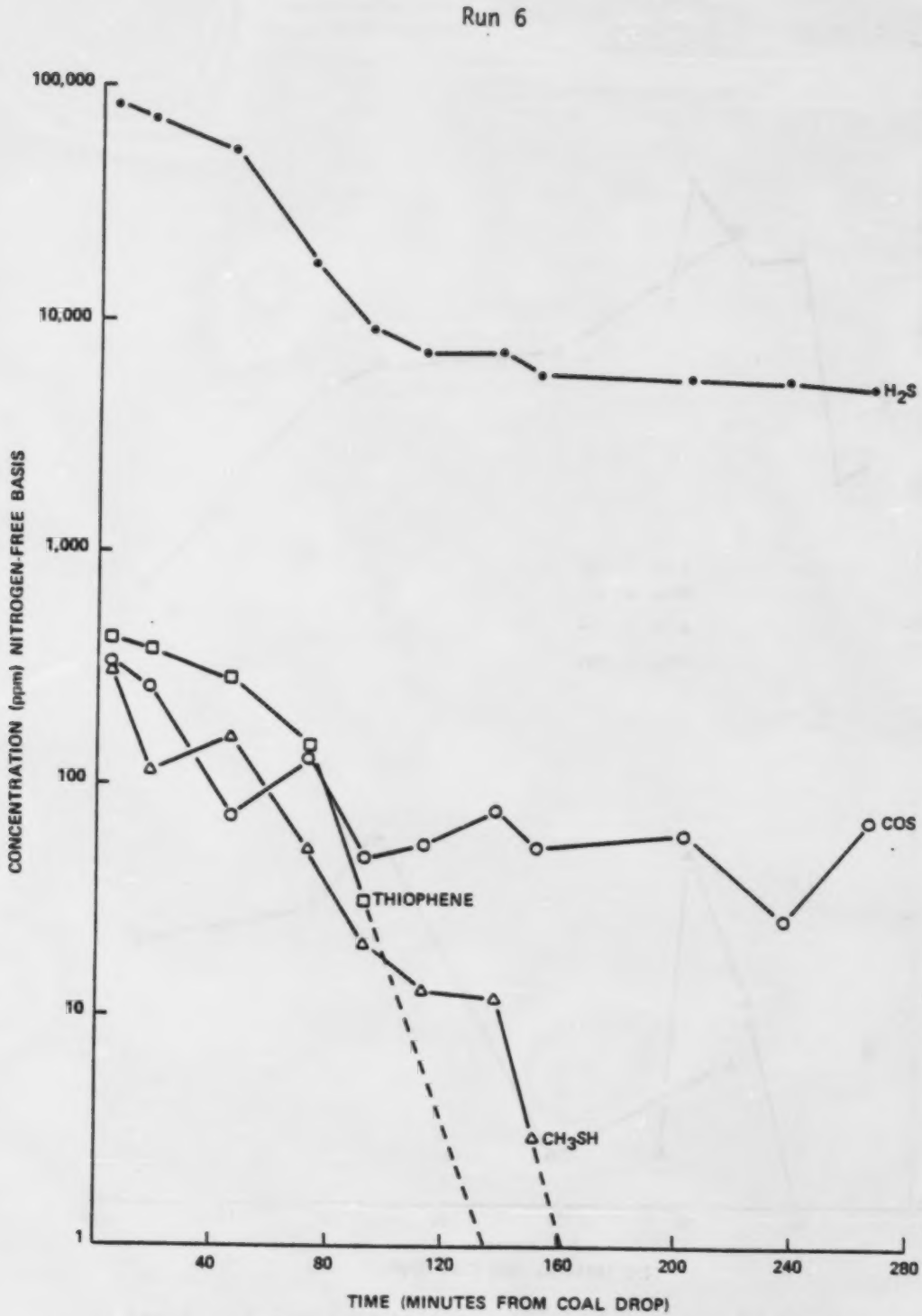


Figure 11. Sulfur-containing gas compositions (coal run 6).

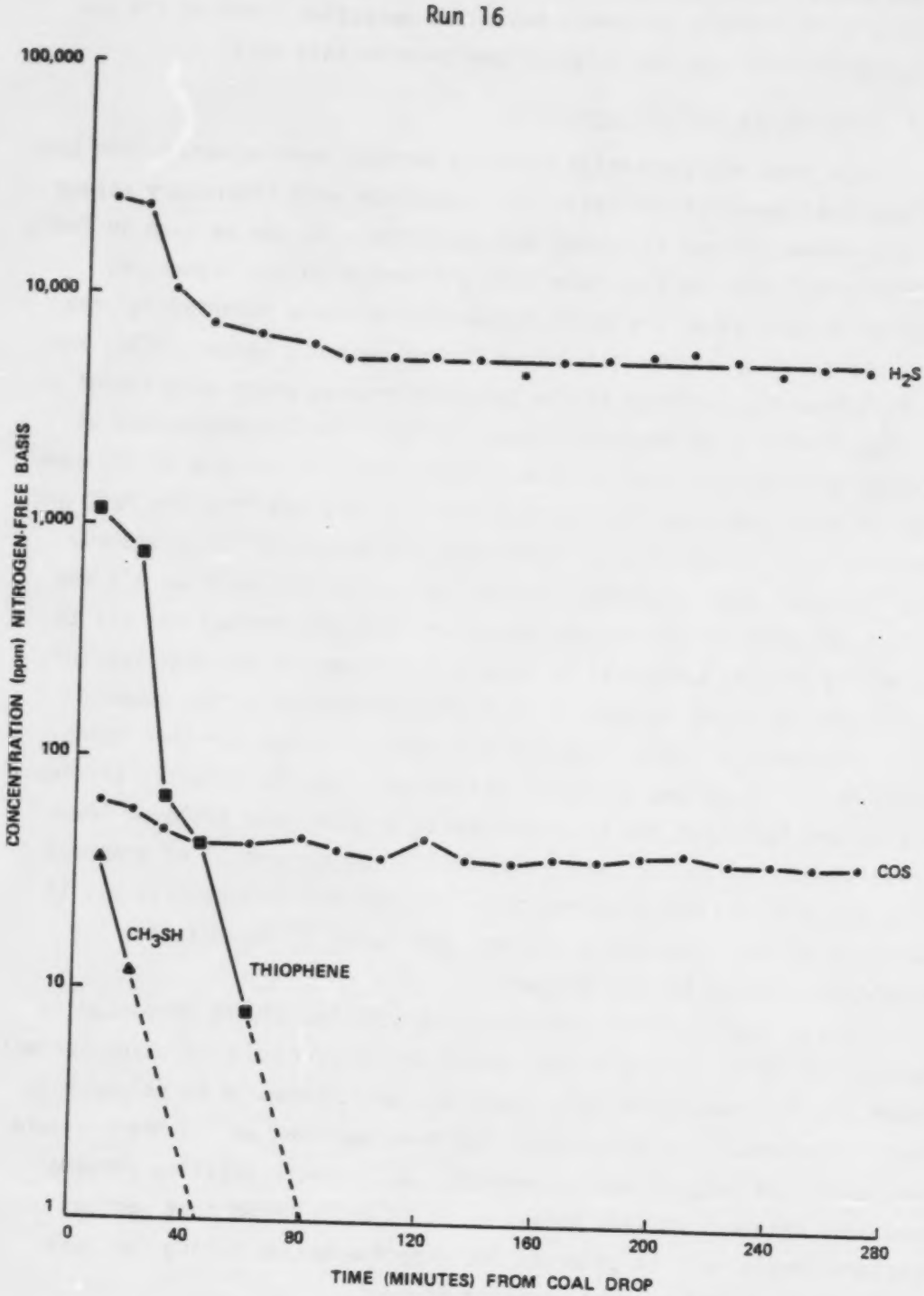


Figure 12. Sulfur-containing gas compositions (coal run 16).

methyl mercaptan and thiophene were detected. As seen in Figures 11 and 12, the methyl mercaptan and thiophene concentrations were found to decrease quite rapidly to levels below the detection limit of the gas chromatograph with the FPD detector employed in this work.

6.1.3 Comparative Gasification Data

Data from representative sampling periods were selected from both char and coal gasification tests for comparison with literature values for both fixed bed and fluidized bed gasifiers. As can be seen in Table 7, the overall results that have been achieved with the laboratory gasifier in this study are quite comparable to those reported for the fixed bed gasifier of the Morgantown Energy Research Center (MERC) and the fluidized bed gasifier of the Synthane process under development at the Pittsburgh Energy Research Center (PERC). The concentrations of hydrogen sulfide, carbonyl sulfide, ethane and ethylene are of the same order of magnitude from the RTI test runs as they are from the MERC and PERC results. It can also be noted that the amount of tar produced, 0.022 kg/kg of coal converted, is the same value for Run 6 at RTI and the MERC reactor. Finally, the amount of fuel gas product was 2.7 to 2.9 Nm^3/kg of coal converted in Runs 6 and 16 and in the MERC reactor.

It can be noted in Table 7 that the hydrogen-to-carbon monoxide ratio is generally higher from the RTI laboratory reactor than those ratios in the other two processes presented. This is directly attributable to the fact that the RTI experiments to date have employed lower air-to-steam feed ratios than those typical of commercial or proposed fixed bed coal gasification reactors. Higher air-to-steam ratios, in the range of the candidate processes, are to be utilized in ongoing parametric studies in this project.

Typical coal gasifier operating characteristics are presented in Table 8 for seven candidate coal gasification processes of major current interest. The results of this study are anticipated to be relevant to these processes. The RTI reactor has been operated at 1.5 MPa pressure throughout the initial tests, however. While representative results have been obtained at this pressure, it is anticipated that various pressure levels will be selected for experimentation during the parametric phase of the current research project.

TABLE 7. COAL GASIFICATION: OPERATING CONDITIONS AND PRIMARY PRODUCTS

Test Run No. Feed Material	No.2 FMC Char Air	No.4 FMC Char External heat only	No.6 Ill.#6 Coal External heat only	No.16 Ill.#6 Air	MERC (Air Blown) Ill.#6 Coal	Synthane (Air Blown) Ill.#6 Coal	Synthane (Oxygen Blown) Ill.#6 Coal
Feed Amount, Kg	0.175	0.600	1.034	1.573	*	*	*
Pressure, MPa	1.5	1.5	1.5	1.5	0.22	1.9	4.2
Temperature (exit)°C	285	353	367	454	650	NA	760
Temperature (max.)°C	735	833	726	955	1350	987	982
Time @ Sample, min	77	123	73	78	--	--	--
Component (MF)							
O_2 (%)	3.0	--	--	--	--	--	--
N_2 + Ar (%)	56.9	27.7	35.1	26.6	51.5	43.4	--
CO (%)	2.0	3.1	4.0	17.0	21.8	10.1	13.2
CO_2 (%)	17.4	20.0	10.1	16.9	6.9	17.9	36.2
H_2 (%)	9.0	38.8	29.4	36.6	17.8	21.5	32.3
CH_4 (%)	4.9	8.9	18.2	2.5	2.0	5.6	15.0
H_2S (%)	1.3	0.6	1.2	0.5	0.2*	0.7*	1.6*
COS (ppm)	63	11	83	33	315	NA	150
C_2H_4 (ppm)	23	47	1000	8	NA	NA	NA
C_2H_6 (ppm)	157	380	4800	37	2000	7000	16000
Tar (kg/kg coal)	--	--	0.022	0.035	0.022	0.047	0.047
Gas Product, Nm^3/kg	12.8	3.5	2.8	2.7	2.9	1.3	0.81
Gas Product, scf/lb	220	56	44.6	43.8	47	20.7	13.8

NA--Not Available
MF--Moisture Free
*Elemental composition of feed coal varies somewhat from that used in the RTI tests.

TABLE 8. TYPICAL COAL GASIFIER OPERATING CHARACTERISTICS

	Wellman-Galusha Fixed-Bed	MERC Stirred Bed Fixed-Bed	Woodall-Duckham Fixed-Bed	U-Gas Fluidized-Bed	BCR Low-Btu Gasifier Three Stage Fluidized-Bed	Synthane* Fluidized-Bed	Combustion Engr. Entrained Flow
Air/Coal Ratio, kg/kg (lb/lb)	3.5 (3.5)	3.0 (3.0)	2.3 (2.3)	3.0 (3.0)	3.2 (3.2)	0.35*(0.35)	3.5 (3.5)
Steam/Coal Ratio, kg/kg (lb/lb)	0.4 (0.4)	0.5 (0.5)	0.25(0.25)	0.5 (0.5)	0.7 (0.7)	1.25 (1.25)	NA
Nominal Pressure, MPa (psia)	0.10(14.7+)	2.1(285)	0.1+(14.7+)	2.5(350)	1.75(235)	7.0 (1000)	0.1+(14.7+)
Exit Gas Temperature, °K (°F)	922 (1200)	922 (1200)	394 (250)	1116 (1550)	1255 (1800)	1033 (1400)	1144 (1600)
Maximum Temperature, °K (°F)	1633 (2400)	1633 (2400)	1477 (2200)	1311 (1900)	1422 (2100)	1255 (1800)	2255 (3600)
Oil and Tar Product, kg/kg coal (lb/ton)	0.06 (120)	0.04 (70)	0.08 (150)	Small	None	0.05 (104)	Negligible
Particulate Product, kg/kg coal (lb/ton)	0.03 (60)	0.03 (60)	Low	Recycled	Fine Ash	0.3 (600)	Small
Gas Product, Nm^3/kg coal (scf/lb coal)	3.8 (64)	3.0 (50)	2.9 (49.7)	3.7 (63)	4.9 (83.3)	0.81 (13.8)	3.9 (66.7)
Higher Heating Value, J/Nm^3 (Btu/scf)	6.0×10^6 (160)	5.2×10^6 (140)	6.5×10^6 (175)	5.7×10^6 (154)	6.0×10^6 (160)	1.3×10^7 (355)	4.7×10^6 (127)
Cold Gas Efficiency, %	75	79	77	79	88	NA	69
Gas Composition, Cold & moisture free							
CO	28.6	20.4	28.3	19.6	25.7	13.2[10.1]**	22.1
CO_2	3.4	8.7	4.5	9.9	5.2	36.2[17.9]	7.0
H_2	15.0	15.5	17.0	17.5	23.4	32.3[21.5]	17.0
CH_4	2.7	2.4	2.7	3.4	--	15.0[5.6]	0.03
N_2 + Ar	50.3	52.5	47.2	48.9	45.5	-- [43.5]	53.3
H_2S + COS	--	0.5	0.3	0.7	0.2	1.6[0.7]	0.6

*Oxygen blown operation typical for Synthane process.
**Gas composition for airblown operation for Synthane process.
NA-not available.

6.2 CHEMICAL ANALYSIS RESULTS

The chemical analysis results which are reported herein should be regarded as preliminary findings. This is because the experimental laboratory reactor and its accessories, the sampling system and the chemical analysis procedures have all been under development during the tests reported to date. Nonetheless, it seems desirable that these results be presented since they have demonstrated: (1) the feasibility of operating the reactor for sufficient time periods at pressure to collect meaningful samples for further chemical analysis; (2) the ability to achieve operating conditions that simulate conditions in commercial or prototype reactor processes; and (3) the efficacy of procedures for systematic analysis of permanent gases and volatile organic compounds, as well as the high molecular weight semivolatile organic compounds contained within the tar products from the reactor. A substantial effort has been required to achieve these results. The operation of reactors at elevated temperatures and pressures is difficult. The large number and high level of complexity of the organic compounds resulting from coal conversion present a particularly challenging analytical task.

6.2.1 Primary Gas Products

The data presented in Figures 7 through 9 showed that the composition of the primary gas stream from the reactor for the runs focused upon herein is well behaved. The results from the gas chromatography analysis of the primary gas product stream account for all of the major components. Figures 10 through 12 showed concentration profiles for the primary sulfur species which were present in the product gas stream for these runs. Generally, the hydrogen sulfide and carbonyl sulfide levels were found to decrease slightly to a steady value after the initial 40 minutes of the reactor operation. However, the methyl mercaptan and thiophene levels were found to decrease quite dramatically during the initial operating time periods.

6.2.2 Volatile Organic Products

Chemical analysis results have been obtained for the volatile organic compounds removed using Tenax or XAD-2 resin cartridges. The samples have been subjected to both qualitative and quantitative evaluation for their primary peaks. Total ion current plots were generated by gas chromatography/mass spectrometry/computer analysis. In spite of their preliminary nature, the following graphs and tables show that the resolution of individual components has been achieved quite successfully by the chemical analysis procedures utilized.

For Run 2, which is a combustion heat run with a coal char, the results are displayed in Figure 13 and Table 9 for a Tenax cartridge collected upstream of an XAD-2 adsorbent. Run 4 is an external heat run using char feed. Figure 14 and Table 10 display the results obtained for this run using an XAD-2 cartridge operating on the raw reactor gas stream. Run 6 is an external heat run using coal. An XAD-2 cartridge result obtained for Run 6 is shown in Figure 15 and Table 11 and can be compared to Figure 14 and Table 10. Over 80 distinct compounds were detected in the effluent from the char feed material as compared with over twice that number from the Illinois No.6 coal.

Also, for Run 6, results of a steady-state XAD-2 cartridge are shown in Figure 16 and Table 12. This sample, which was collected during the char gasification stage of the conversion process, i.e., after the devolatilization stage, shows some 20 prominent organic constituents as compared with some 60 found during the devolatilization stage.

Run 16 also utilized Illinois No.6 coal. This run employed an air-to-steam rate of approximately 0.5 on a weight-to-weight basis. The analytical chemical results for volatile organic compounds obtained for this run are presented in Figures 17 and 18 and Tables 13 and 14 for a Tenax and a steady-state XAD-2 cartridge, respectively. It was found that a somewhat greater amount of volatile organic material resulted from Run 6 than from Run 16. It is believed that this is due to the fact that in Run 16 the oxidative process associated with the air feed was responsible for reducing volatile organic material loading of the effluent gas stream.

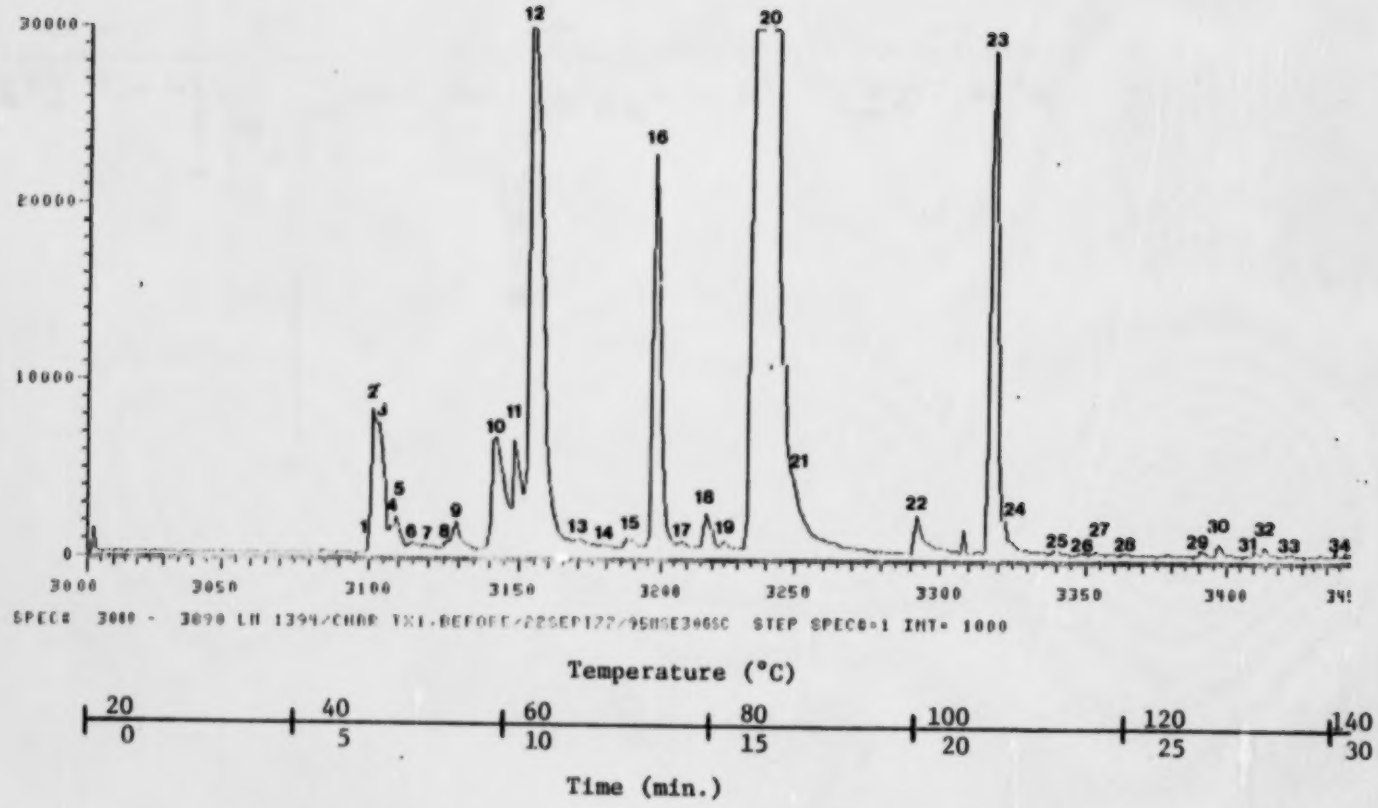


Figure 13. Total ion current chromatogram of GC/MS analysis of upstream Tenax sample for char run 2.

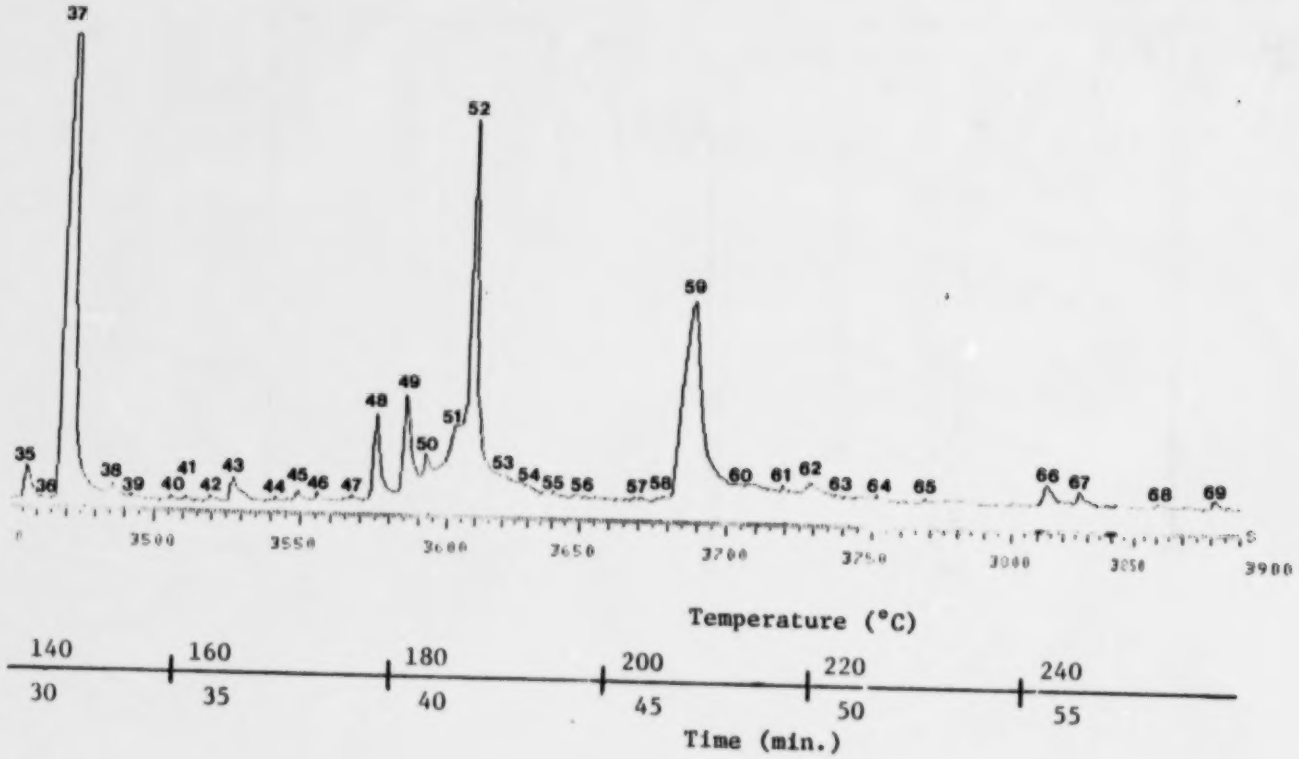


Figure 13 (cont'd)

TABLE 9. COMPOUNDS IDENTIFIED FROM TENAX SAMPLE UPSTREAM OF XAD-2 CHAR RUN 2

Chromatographic Peak No.	Elution Temp. (°C)	Compound
1	47	CO_2
4	49	carbonyl sulfide
5	50	sulfur dioxide
7	52	butane isomer
8	55	acetaldehyde
9A	58	acetonitrile
10	59	acetone
11	61	diethyl ether
12	63	dichloromethane (BKG)
12A	65	carbon disulfide (tent)
13	67	C_4H_8O isomer (tent)
14	69	2-methylpentane
15	71	3-methylpentane
15A	73	hexafluorobenzene (eS)
16	74	n-hexane
17	77	ethyl acetate
17A	78	C_7H_{16} isomer
18	80	methylcyclopentane
19	82	perfluorotoluene (eS)
19A	83	$C_5H_{10}O$ isomer (tent)
20	84-7	benzene
20A	87	thiophene
21A	92	trichloroethylene (BKG)
21B	94	C_7H_{16} isomer (tent)
21C	95	C_7H_{16} isomer
22	100	acetic acid
23	107	toluene
24	109	methylthiophene isomer (tent)
24A	110	methylthiophene isomer
25	113	$C_6H_{12}O$ isomer
26	115	n-octane (tent)
26A	116	C_8H_{16} isomer
27	117	tetrachloroethylene (BKG)
29	127	ethylbenzene
30	129	xylene isomer
31	132	styrene
32	133	o-xylene
32A	136	C_9H_{18} isomer
33	136	n-nonane
33A	139	isopropylbenzene (tent)
35	145	benzaldehyde
36	147	C_3-alkyl benzene isomer
36A	148	C_3-alkyl benzene isomer
37	149	benzonitrile
37A	150	phenol
37B	151	methylstyrene isomer (tent)
37C	151	C_3-alkyl benzene isomer (tent)
37D	152	methylstyrene isomer
38	153	benzofuran + C_3-alkyl benzene
-	-	isomer
39	155	n-decane
39A	155	C_4-alkyl benzene isomer (tent)
39B	156	dichlorobenzene isomer (BKG)
40	159	C_3-alkyl benzene isomer
41	160	sat. hydrocarbon
41A	161	indan
42	163	indene
43	165	acetophenone
43A	166	cresol isomer
43B	167	C_4-alkyl benzene isomer
45	170	n-nonanal
46	172	n-undecane
47	176	C_2-alkyl phenol + C_4-alkyl
-	-	benzene (tent) isomers
48	178	dimethylphenol isomer
49	181	C_2-alkyl phenol isomer
50	183	C_2-alkyl phenol isomer
51	186	benzoic acid + 2-(p-tert-bu-
-		tylphenoxy)ethanol (tent)
52	187	naphthalene
52A	188	2,3-benzothiophene
53	190	C_3-alkyl phenol isomer
54	192	C_3-alkyl phenol isomer
55	195	C_3-alkyl phenol isomer
57	204	β-methylnaphthalene
58	206	α-methylnaphthalene
59	209	benzamide
61	218	$C_{14}H_{30}$ isomer
65	231	sat. hydrocarbon

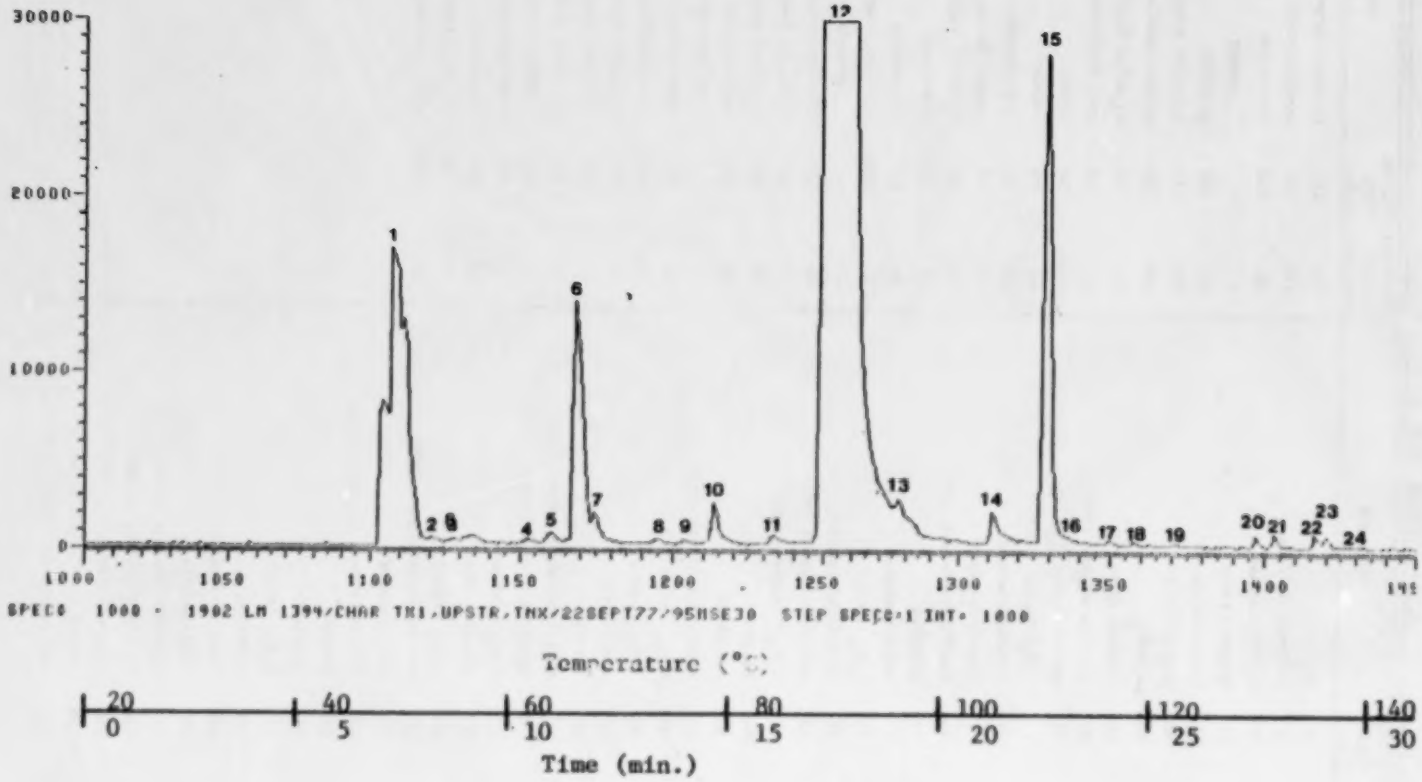


Figure 14. Total ion current chromatogram of GC/MS analysis of upstream Tenax sample for char run 4.

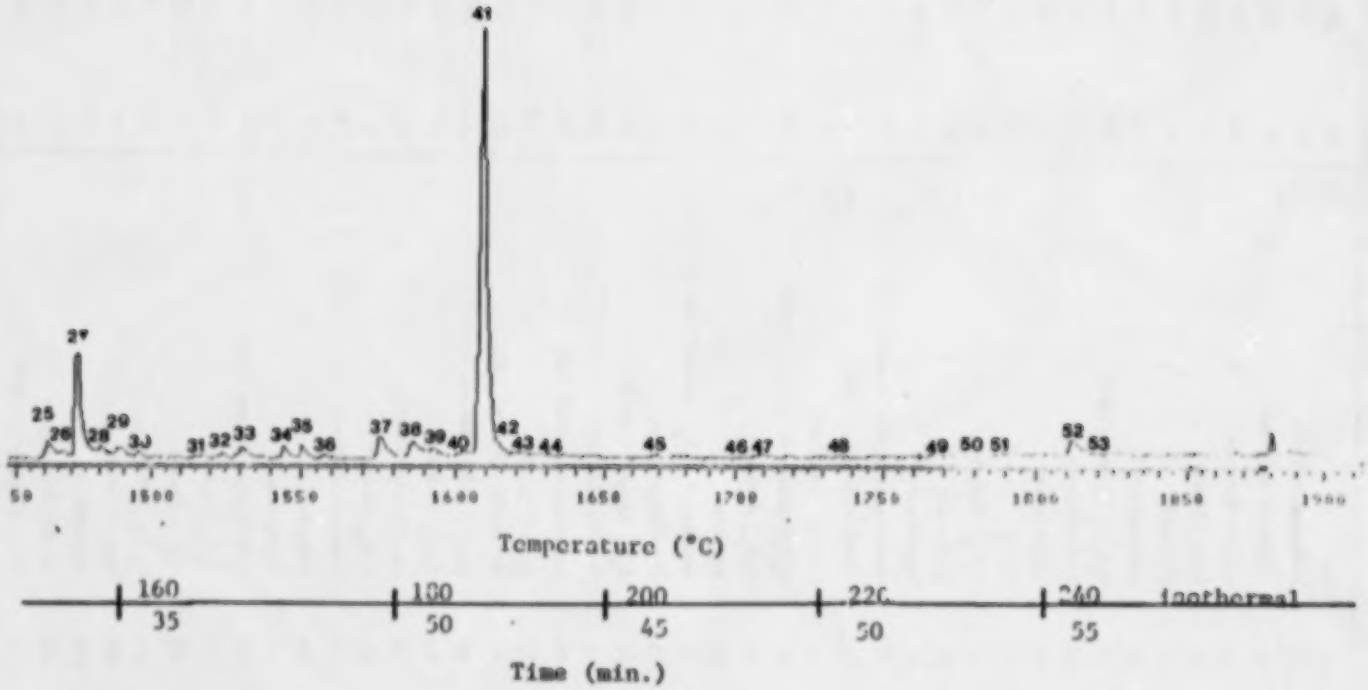


Figure 14 (cont'd).

TABLE 10. COMPOUNDS IDENTIFIED FROM TENAX SAMPLE UPSTREAM OF XAD-2, CHAR RUN 4

Chromatographic Peak No.	Elution Temp. (°C)	Compound
1	49	CO_2
1A	50	hydrogen sulfide
1B	51	carbonyl sulfide
2	55	sulfur dioxide
3	57	C_4H_8 isomer
3A	57	n-butane
3B	58	methanethiol
3C	58	$C_2H_6S_2$ isomer (tent)
3D	59	acetaldehyde
3E	62	isopentane
4A	63	furan
4B	63	C_3H_{10} isomer
5	64	n-pentane
5A	65	acetonitrile
5B	65	dichloroethylene isomer (BEC)
6	66	dichloromethane (BEC)
7	68	carbon disulfide
7A	69	C_4H_8O aldehyde isomer (tent)
7B	69	C_7H_{16} isomer
7C	70	acetone
7D	72	butanal + C_7H_{16} isomer (tent)
8	73	2-methylpentane
8A	74	C_6H_8 isomer (tent)
9	76	3-methylpentane
9A	78	hexafluorobenzene (sE)
10	79	n-hexane
10A	80	chloroform (tent) (BEC)
10B	82	methyl ethyl ketone (tent)
10C	83	C_7H_{16} isomer
11	84	methylcyclopentane
11A	85	C_7H_{16} isomer
11B	88	perfluorotoluene (sE)
12	89	benzene
12A	92	thiophene
13	96	trichloroethylene (BEC)
13A	98	C_7H_{16} isomer
13B	101	C_8H_{16} isomer
13C	104	C_8H_{16} isomer
14	106	acetic acid
15	111	toluene
16	112	methylthiophene
16A	112	$C_6H_{12}O$ isomer (tent)
16B	114	C_8H_{18} isomer (tent)
17	116	hexanal
18	118	n-octane
18A	119	tetrachloroethylene (tent) (BEC)
20	129	ethylbenzene
21	131	xylene isomer
22	135	styrene
22A	135	n-heptanal
23	136	p-xylene
24	138	C_9H_{18} isomer
24A	138	C_9H_{20} isomer
24B	142	isopropylbenzene
24C	146	$C_{10}H_{22}$ isomer
25	147	benzaldehyde
25A	147	n-propylbenzene
26	148	ethyltoluene isomer
27	150	benzonitrile
27A	151	phenol
27B	152	methylstyrene + $C_{10}H_{22}$ (tent)
-	-	isomers
28	152	2-octanone
28A	154	methylstyrene isomer +
-	-	n-octanal
29	154	benzofuran
29A	155	C_3-alkyl benzene isomer
30	156	n-decane
30A	159	C_4-alkyl benzene isomer
30B	160	C_3-alkyl benzene isomer
30C	160	C_4-alkyl benzene isomer
30D	161	$C_{11}H_{24}$ isomer
31	162	indan
31A	163	indene
32	164	C_4-alkyl benzene isomer
32A	165	C_4-alkyl benzene isomer
33	166	acetophenone
33A	167	cresol isomer
34	170	methylindan or C_4H_7-benzene
-	-	isomer
35	171	n-nonanal
35A	173	C_3-alkyl benzene isomer
36	173	n-undecane
36A	176	C_2-alkyl phenol isomer
37	178	dimethylphenol isomer
37A	178	$C_{13}H_{26}$ isomer (tent)
37B	179	dimethylphenol isomer
38	181	C_2-alkyl phenol isomer
39	183	C_2-alkyl phenol isomer
40	186	C_3-alkyl phenol isomer
41	188	naphthalene
41A	189	2,3-benzothiophene

Table 10 (cont'd)

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
42	190	n-dodecane
43	192	C_3-alkyl phenol isomer
43A	193	C_3-alkyl phenol isomer
44	195	C_3-alkyl phenol isomer
44A	197	propiophenone
44B	201	undecanal (tent)
45	204	β-methylnaphthalene
45A	206	α-methyl naphthalene
46	211	dodecanal (tent)
47	215	biphenyl
47A	216	n-tridecane (tent)
48	222	$C_{14}H_{28}$ isomer
48A	227	C_2-alkyl naphthalene isomer
49	230	unsat. hydrocarbon

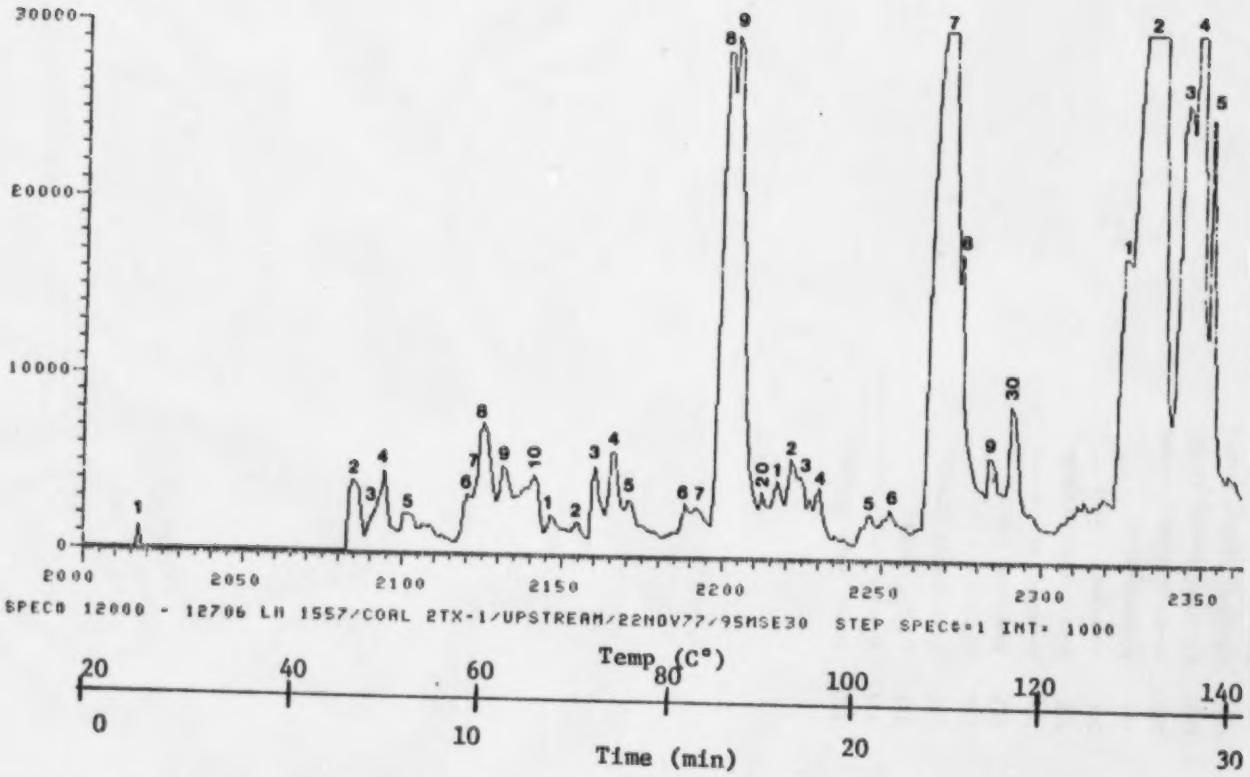


Figure 15. Total ion current chromatogram of GC/MS analysis of upstream Tenax sample for coal run 6.

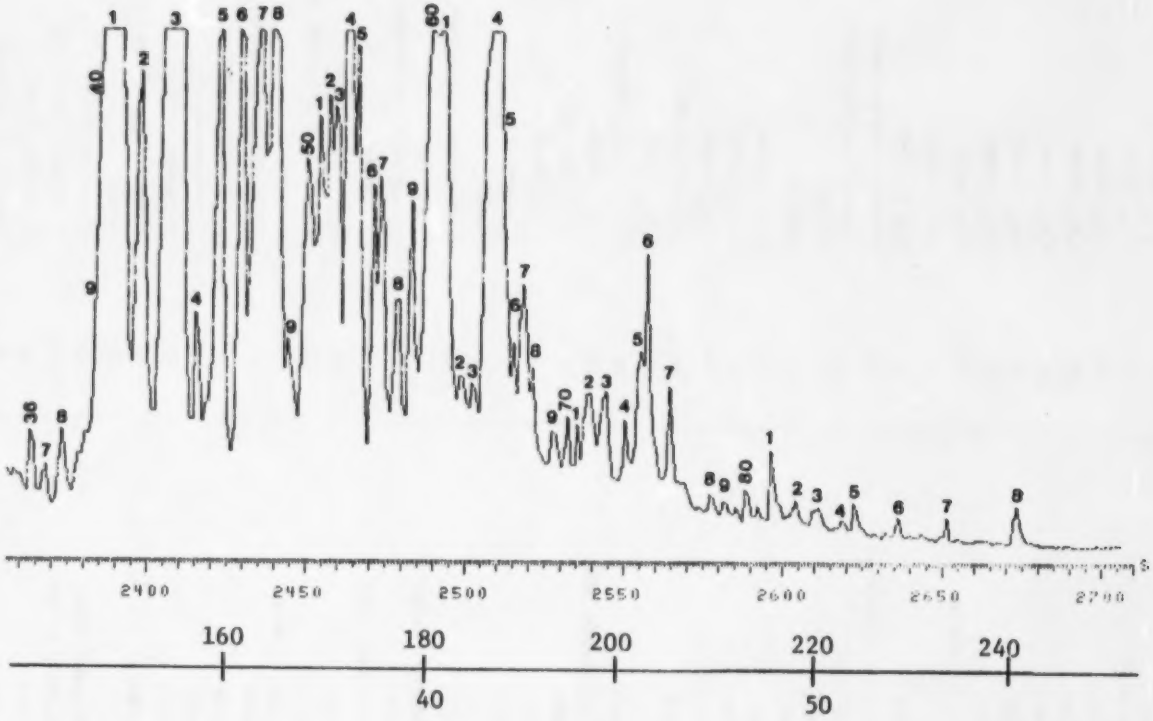


Figure 15 (cont'd)

TABLE 11. COMPOUNDS IDENTIFIED FROM THE UPSTREAM TENAX SAMPLE FROM COAL RUN 6

Chromatographic Peak No.	Compound	µg/ℓ
2	carbon dioxide	
3	carbonyl sulfide	
4	sulfur dioxide	
5	butene isomer	
5a	butene isomer	
5b	C_5H_{12} isomer	
6	C_5H_{10} isomer	
7	unsaturated hydrocarbon	
8	acetone	
9	C_5H_{10} isomer	
9a	carbon disulfide + methylene chloride (BEC)	
10	C_5H_6 isomer	
11	C_5H_6 isomer	
11a	C_5H_8 isomer	
12	C_5H_{10} isomer	
13	methyl ethyl ketone	
13a	C_6H_{12} isomer	
15	n-hexane	
15a	C_6H_{12} isomer	
15b	C_6H_{12} - C_7F_8 isomers (eE)	
16	C_6H_{12} isomer	
17	C_6H_8 isomer	
17a	C_6H_{10} isomer	
18	benzene	7.7
19	thiophene	1.3
20	methyl isopropyl ketone	
21	2-pentanone	
22	trichloroethylene (BEC)	
22a	C_7H_{14} isomer	
23	n-heptane	
24	C_7H_{14} + C_7H_{12} isomers	
24a	C_7H_{12} isomer	
25	C_7H_{14} isomer	
25a	acetic acid	
26	C_7H_{10} isomer	
26a	C_7H_{12} isomer	
27	toluene	5.7
27a	methylthiophene isomer	10.1
28	methylthiophene isomer	0.9
28a	C_8H_{16} isomer	
29	C_8H_{16} isomer	
29a	C_8H_{16} isomer	
30	n-octane	
30a	C_8H_{16} isomer	
30b	C_8H_{16} isomer	
30c	C_8H_{14} isomer	
30d	C_8H_{14} isomer	
30e	C_8H_{14} isomer	
30f	C_9H_{22} isomer	
30g	C_8H_{16} isomer	
30h	C_8H_{16} isomer	
30i	C_9H_{18} isomer	
30j	C_9H_{12} isomer	
31	ethylbenzene	0.8
32	xylene isomer	6.2
32a	dimethylthiophene isomer	1.8
32b	dimethylthiophene isomer	11
33	styrene	2.9
34	o-xylene	3.7
34a	C_2-thiophene	2.3
35	C_9H_{20} isomer	
35a	C_9H_{18} isomer	
36	isopropylbenzene	
37	C_9H_{16} isomer	
38	C_9H_{18} + $C_{10}H_{22}$ isomers	
38a	$C_{10}H_{22}$ isomer	
39	n-propylbenzene	
39a	C_3-thiophene	
40	C_3-benzene	
41	phenol	1.9
41a	C_3-thiophene + C_3-benzene isomers	
42	C_3-benzene + C_3H_5-benzene isomers	
42a	C_3-thiophene isomer	6.5
43	benzofuran + C_3-benzene isomer	
43a	n-decane	
44	2,3,4-trimethylthiophene	
44a	C_4-thiophene isomer	
44b	C_4-benzene isomer	
45	C_3-benzene isomer	
46	cresol + C_3H_5-benzene isomers	
47	indene	19.5
47a	C_4-benzene isomer	
47b	C_4-benzene isomer (tent)	
48	C_4-benzene isomer	
48a	cresol + C_4-thiophene isomers	
48b	C_4-benzene isomer	
49	C_4-thiophene isomer	
50	C_4-benzene isomer	
50a	C_4H_7-benzene	

Table 11 (cont'd)

Chromatographic Peak No.	Compound	µg/ℓ
51	C_4-benzene isomer	
51a	C_4H_7-benzne	
52	$C_{11}H_{22}$ isomer	
52a	C_2-phenol	
53	methyl benzofuran isomer	0.4
53a	$C_{11}H_{24}$ isomer	
54	methyl benzofuran isomer	4.1
54a	C_4-benzene	
55	C_5-benzene + $C_{11}H_{22}$ isomers	
56	C_4-benzene isomer	
57	C_4H_7-benzene isomer	
58	C_2-phenol isomer	
58a	C_5-benzene isomer	
59	C_4H_7-benzene isomer	
59a	C_5-benzene isomer	
59b	C_4-thiophene isomer	
59b	C_4-thiophene isomer	
59c	ethylphenol isomer	
60	methyl indene isomer	
60a	C_4H_7-benzene isomer	5.6
60b	C_4-benzene isomer	
60c	methyl indene isomer	6.1
61	C_5-benzene isomer	
62	C_2-phenol isomer	
62a	C_5H_9-benzene isomer	
63	benzoic acid	
63a	C_5H_9-benzene isomer	
64	naphthalene	35
64a	C_5H_9-benzene isomer	
64b	2,3-benzothiophene + n-dodecane + C_5-benzene isomer	3.7
64c	C_5H_9-benzene isomer	
65	dimethylbenzofuran isomer	1.2
66	$C_{13}H_{28}$ isomer	
67	dimethylbenzofuran isomer	
68	C_6-benzene isomer	
69	C_5H_9-benzene isomer	
70	methyl dihydronaphthalene isomer	
71	C_5H_9-benzene isomer	
72	methyl dihydronaphthalene isomer	
72a	C_5H_9-benzene isomer	
73	$C_{14}H_{30}$ isomer	
73a	$C_{12}H_{16}$ isomer	
74	$C_{13}H_{26}$ + C_5H_9-benzene isomers	
74a	$C_{14}H_{28}$ + methylbenzothiophene isomers	
75	tridecane	
76	β-methylnaphthalene	4.9
76a	C_6H_{11}-benzene isomer	
76b	methylbenzothiophene isomer	
77	α-methylnaphthalene	
77a	C_6H_4-benzene isomer (tent)	
78	C_6H_{11}-benzene isomer	
79	$C_{14}H_{30}$ isomer	
80	$C_{13}H_{32}$ isomer	
80a	hydrocarbons	
81	n-tetradecane	
81b	ethyl-naphthalene isomer	
82	dimethylnaphthalene isomer	
83	dimethylnaphthalene isomer	
84	dimethylnaphthalene isomer	
85	$C_{16}H_{34}$ isomer + biphenylene	
85a	C_2-naphthalene isomer	
86	n-pentadecane + acenaphthene	
86a	C_3-naphthalene isomer	
87	dibenzofuran + C_8H_{15}-benzene isomers	0.07
87a	C_3-naphthalene isomer	
87b	C_3-naphthalene isomer	

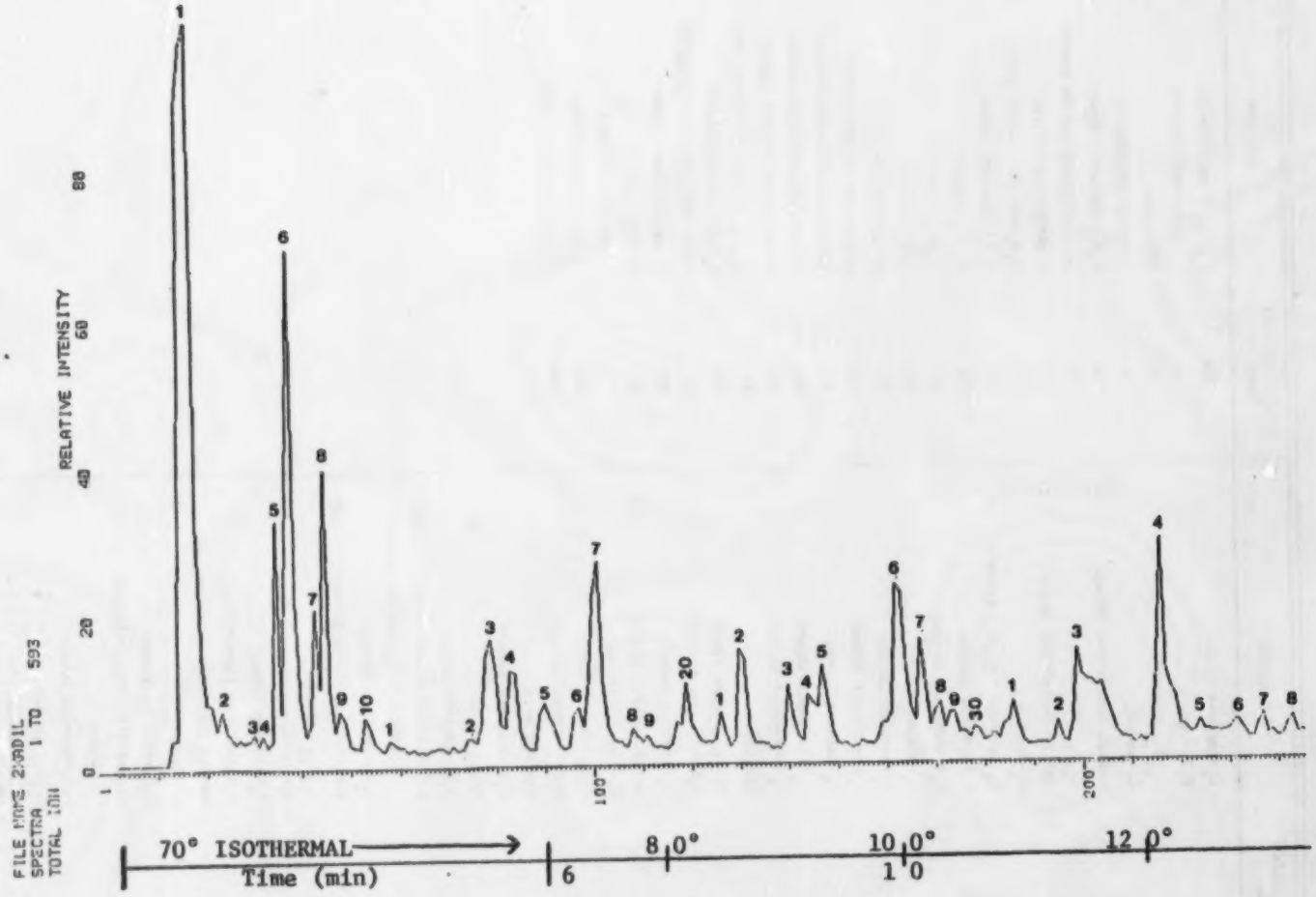


Figure 16. Total ion current chromatogram of GC/MS analysis of steady-state XAD-2 sample for coal run 6.

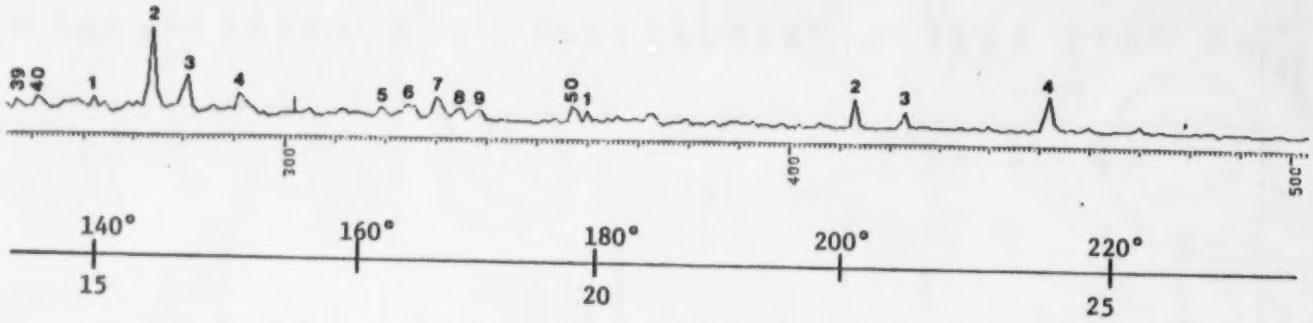


Figure 16 (cont'd).

TABLE 12. COMPOUNDS IDENTIFIED FROM THE STEADY-STATE XAD SAMPLE FROM COAL RUN 6

Chromatographic Peak No.	Compound	mg
1	toluene	
2	C_8H_{18} isomer	
2a	C_8H_{14} + dichloromethane (bkg)	
3	C_8H_{16} isomer	
4	C_9H_{18} isomer	
5	ethylbenzene + ethylthiophene	> 30
6	dimethylthiophene + xylene isomers	> 30
7	styrene	
8	xylene isomer	> 30
8a	dimethylthiophene isomer	> 30
9	C_9H_{18} isomer	
10	n-nonane	
10a	unsaturated hydrocarbons	
11	C_3-benzene isomer	
11a	C_9H_{16} isomer	
11b	C_9H_{16} isomer	
11c	C_9H_{18} isomer	
11d	C_3H_3-benzene isomer	
11e	$C_{10}H_{22}$ isomer	
12	C_3-benzene isomer	18
12a	unsaturated hydrocarbons	
12b	C_3-thiophene isomer	
13	C_3-benzene isomer	19
13a	C_3-thiophene isomer	
14	C_3-benzene isomer	7.4
14a	C_3-thiophene	
15	C_3-benzene + trimethylthiophene	5.8
15a	unknown	
16	benzofuran	
16a	methylstyrene isomer	
17	C_3-benzene isomer	27
17a	phenol	40
18	$C_{10}H_{20}$ isomer	
19	trimethylthiophene isomer	
19a	$C_{10}H_{22}$ isomer	
20	C_3-benzene isomer	6.8
20a	diethylbenzene	
21	indan	7.4
22	indene	110
23	C_4-benzene isomer	7.1
23a	C_4-benzene isomer	
24	C_4-benzene isomer	7.4
24a	cresol isomer	45
25	C_4-benzene isomer	10
25a	C_4-thiophene + cresol isomer	45
25b	C_4-benzene isomer	
25c	C_4-thiophene isomer	
25d	C_4H_7-benzene isomer	
25e	C_4-thiophene + methylindene isomers	
25f	1,2-dimethyl ethylbenzene isomer	
26	C_4H_7-benzene isomer	
26a	C_4-benzene isomer	38
26b	cresol isomer	70
27	C_4H_7-benzene isomer	15
28	methylbenzofuran isomer	
29	methylbenzofuran isomers	
29a	C_4-thiophene isomer	
29b	C_4-benzene isomer	
29c	C_5-benzene + C_2-phenol isomer	20
29d	$C_{11}H_{22}$ isomer	
30	methylindene isomer	
30a	C_4H_7-benzene isomer	
30b	C_4-benzene isomer	
31	$C_{11}H_{24}$ isomer	
31a	C_4H_7-benzene isomer	
31b	C_5H_9-benzene isomer	
31c	$C_{11}H_{22}$ + C_4H_7-benzene isomers	
31d	$C_{11}H_{24}$ isomer	
32	methyl-2,3-dihydroindene isomer	
32a	C_5-benzene isomer	
33	methylindene isomer	57
33a	C_4H_7-benzene + C_5-benzene isomers	
33b	C_4-benzene	
33c	methylindene isomer	40
33d	C_2-phenol isomer	270
33e	n-pentylbenzene	
33f	C_5-thiophene isomer	
33g	C_5-benzene isomer	
33h	C_5H_9-benzene isomer	
34	naphthalene	84
34a	C_2-phenol + unknown	230
35	dimethylindan isomer	
35a	C_6-benzene isomer	
35b	C_5H_9-benzene + C_2-phenol isomers	
35c	C_3-phenol + dimethylbenzofuran	

Table 12 (cont'd)

Chromatographic Peak No.	Compound	ng
36	C_5-benzene + dimethylbenzofuran isomers	
36a	C_2-phenol isomer	
37	dimethyl benzofuran isomer (tent)	
37a	C_5H_9-benzene isomer (tent)	
37b	alkyl benzene isomer	
38	$C_{12}H_{26}$ isomer	
38a	C_6-benzene + C_3-phenol isomers	
39	C_3H_9-benzene isomer	
39a	C_3-phenol isomer	
39b	$C_{13}H_{28}$ isomer	
40	C_3-phenol isomer	
40a	dimethylindan isomer	
40b	$C_{11}H_{12}$ isomer	
41	C_5H_9-benzene isomer	
41a	C_3-phenol isomer	
41b	C_3-phenol isomer	
41c	methylbenzothiophene isomer (tent)	
41d	C_5H_9-benzene isomer	
42	β-methylnaphthalene	0.6
42a	methyl benzothiophene isomer (tent)	
42b	C_6H_{11}-benzene isomer	
42c	methyl benzothiophene isomer (tent)	
42d	C_6H_4-benzene isomer	
43	α-methylnaphthalene	tr
43a	saturated hydrocarbon	
43b	C_6H_{11}-benzene or unknown	
44	n-tridecane	
44a	C_6H_{11}-benzene or unknown	
44b	saturated hydrocarbon	
44c	$C_{14}H_{26}$ isomer	
44d	$C_{14}H_{28}$ isomer	
44e	biphenyl	0.6
44f	dimethyl-1-thiaindene isomer (tent)	
45	ethylnaphthalene isomer	
45a	dimethyl thiaindene isomer (tent)	
46	dimethyl naphthalene isomer	
46a	saturated hydrocarbon	
46b	trimethyl tetrahydrophthalene isomer	
47	dimethyl naphthalene isomer	
48	n-tetradecane	
48a	dimethyl naphthalene	
49	acenaphthalene	
49a	dimethyl naphthalene isomer	
49b	hydrocarbons	
49c	acenaphthene	0.35
49d	$C_{13}H_{12}$ isomer	
50	$C_{14}H_{14}$ isomer	
50a	$C_{13}H_{12}$ isomer	
51	n-hexadecane	
51a	C_3-naphthalene isomer	
51b	dibenzofuran (tent)	2.7
51c	saturated hydrocarbon	
51d	C_3-naphthalene isomer	
51e	C_3-naphthalene isomer	
51f	fluorene	
51g	$C_{13}H_{12}$ isomer	
51h	hydrocarbon	
51i	$C_{13}H_{10}O$ isomer	
52	$C_{16}H_{18}$ isomer	
53	$C_{16}H_{18}$ isomer	
53a	saturated hydrocarbon	
53b	anthracene	0.1
54	d_{10} anthracene	S
54a	$C_{18}H_{22}$ isomer	
54b	$C_{18}H_{22}$ isomer	

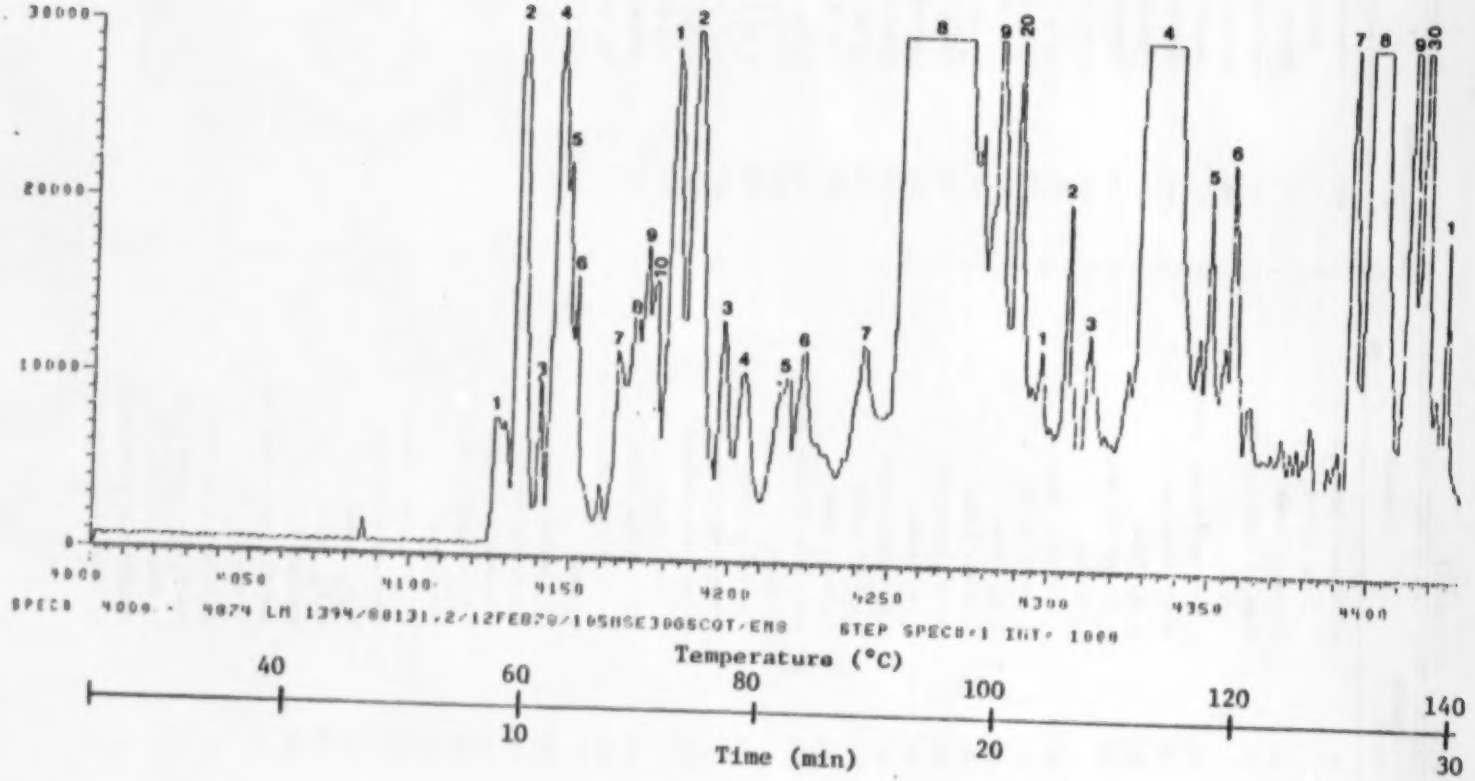


Figure 17. Total ion current chromatogram of GC/MS analysis of Tenax sample 2 for coal run 16.

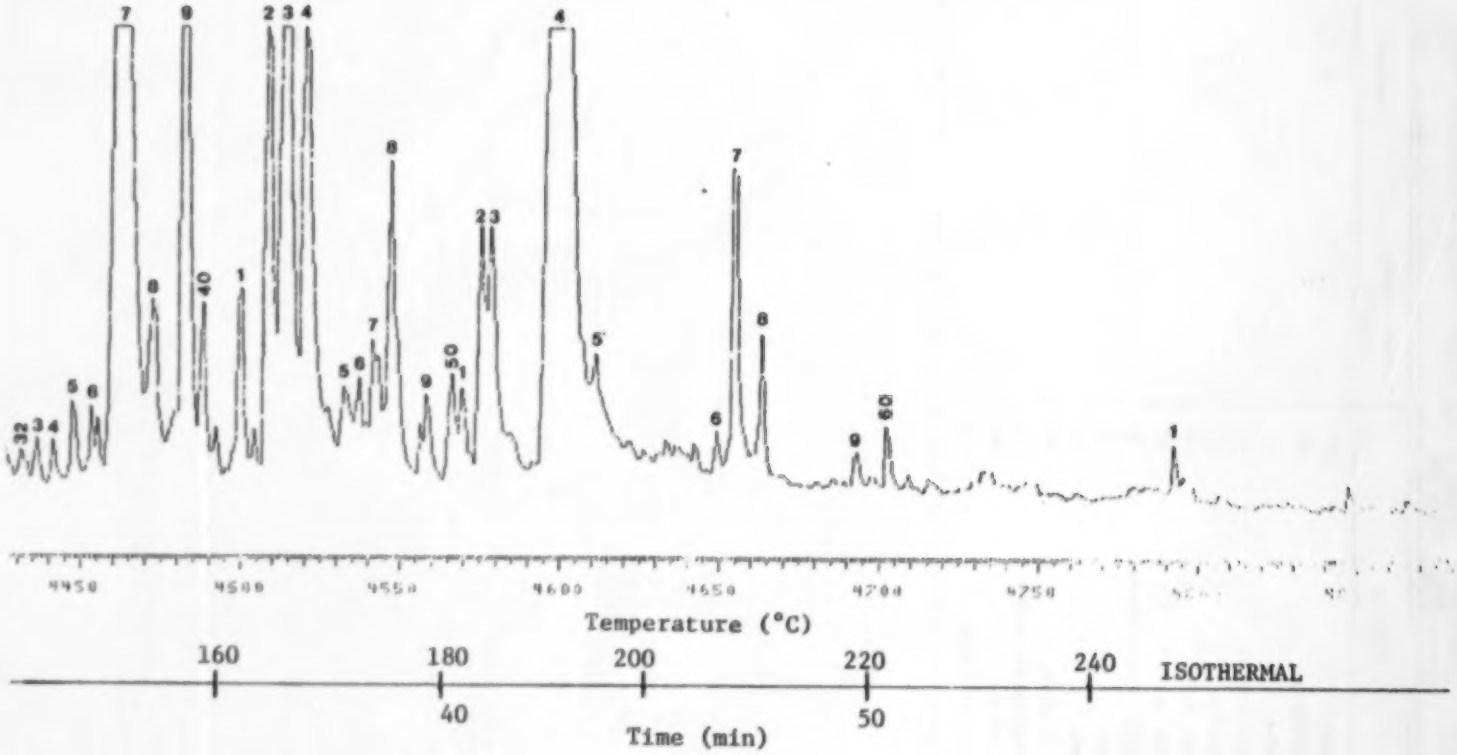


Figure 17 (cont'd).

TABLE 13. COMPOUNDS IDENTIFIED FROM TENAX CARTRIDGE NO.2 FROM COAL RUN 16.

Chromatographic Peak No.	Compound	µg/l	Chromatographic Peak No.	Compound	µg/l
18a	benzene	1100			
18b	thiophene	150			
24a	toluene	125			
24b	methylthiophene	110			
27	ethylbenzene	12			
28	xylene, m,p-	> 40			
30	xylene, o-	12			
37	isopropylbenzene (cumene)	52			
42	indan	8			
43	indene	125			
44	cresol isomer	43			
44b	C_4-alkylbenzene isomer	2			
54	naphthalene	81			
57	2,3-benzothiophene	1			

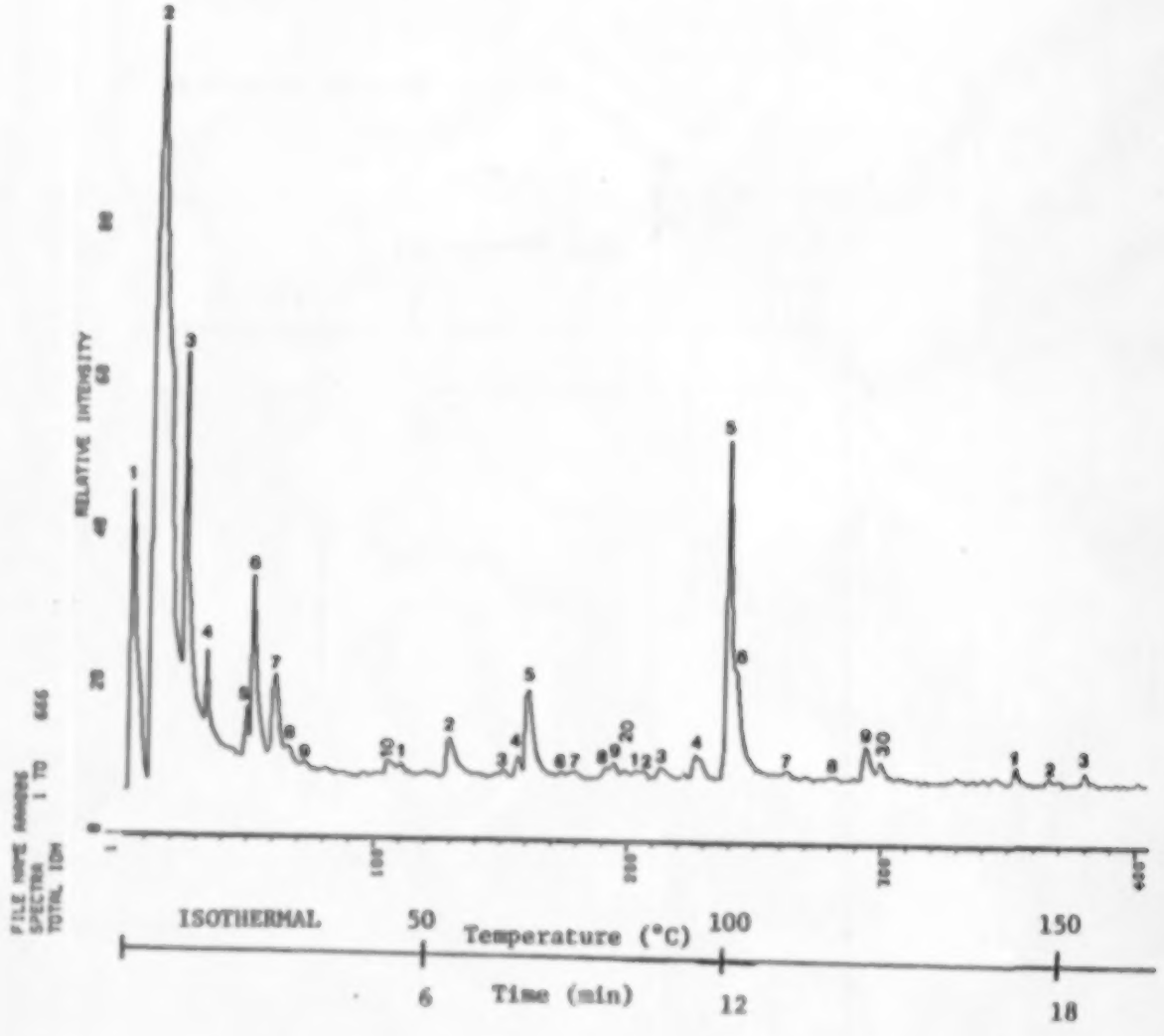


Figure 18. Total ion current chromatogram of GC/MS analysis of steady-state XAD-2 sample for coal run 16.

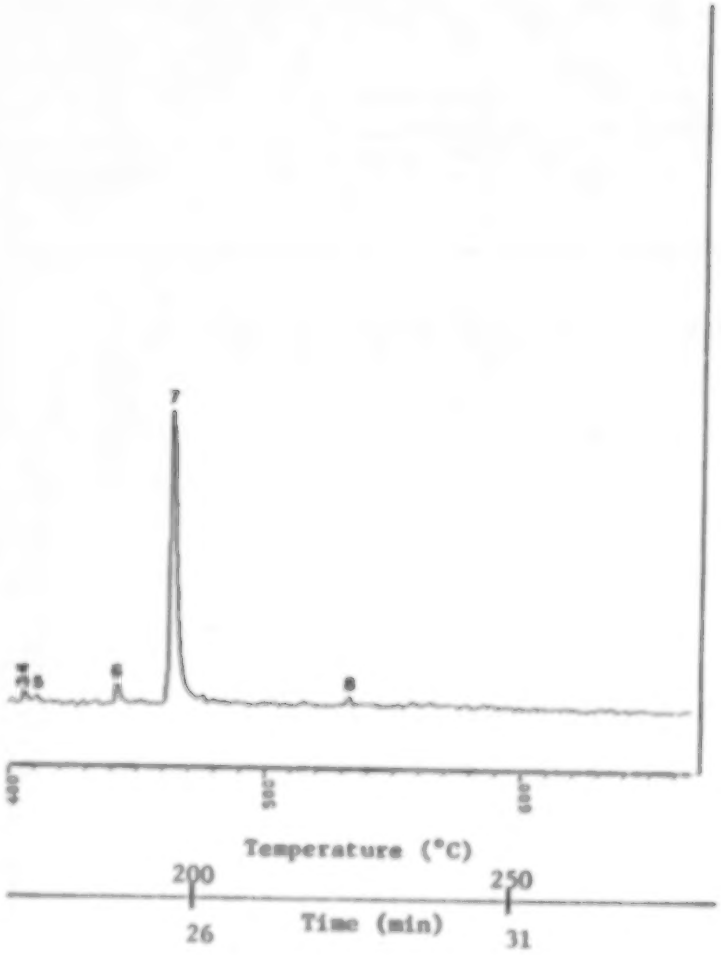


Figure 18 (cont'd).

TABLE 14. COMPOUNDS IDENTIFIED IN THE EXTRACT OF STEADY STATE XAD TRAP FROM COAL RUN 16.

Chromatographic Peak No.	Compound	ng
5	ethylbenzene	2.0
6	m,p-xylene	6.8
	dimethylthiophene isomer	0.6
7	o-xylene + styrene	1.6
8	BEC + dimethylthiophene isomer	0.9
9	C_9H_{12} isopropylthiophene	
10	isopropylbenzene	0.4
11	C_3-benzene	0.3
	C_3-thiophene isomers	
	benzofuran	
12	C_3-benzene	0.3
13	C_3-benzene	0.2
14	indan	1.6
15	indene + phenol	24 3.8
16	diethylbenzene	1.8
17	C_4-benzene	1.9
18	C_4-benzene	tr
19	C_4H_7-benzene + o-cresol	1.4
20	C_4H_7-benzene	
21	methyl-benzofuran	
22	methyl-benzofuran (tent)	
23	hydrocarbon + m,p-cresol	3.4
24	naphthalene trace	6.1
25	naphthalene	41.6
26	benzothiophene + dimethylphenol	9.7
27	dimethylphenol + 3,6-dimethylbenzofuran (tent)	8.0
28	methyl-dihydronaphthalene	
29	β-methylnaphthalene	1.9
30	α-methylnaphthalene	1.0
	biphenyl	0.9
	dimethylnaphthalene	
31	biphenylene	
32	acenaphthalene	0.7
33	dibenzofuran	1.4
	fluorene	0.2
34	$C_2H_4S_3$ or unknown	
35	BEC	
36	BEC	
37	anthracene + d_{10} anthracene	0.1
38	hydrocarbon	
	fluoranthene	< 0.1
	pyrene	< 0.1

A summary of quantitative chemical analysis results obtained by utilizing Tenax and XAD-2 resin adsorbers is presented in Table 15. This table indicates that the Tenax cartridges are more effective than XAD-2 resins for the removal of compounds having a higher volatility, e.g., benzene, thiophene, and toluene. Alternatively, the XAD-2 resins function quite effectively in the capture of high molecular weight organic materials, e.g., naphthalene, biphenyl and anthracene. The results for Run 16 which are shown in Table 15 have been plotted for visualization and comparison. These are shown in Figure 19. Generally, it was found that these concentrations decreased monotonically from the high value detected in the initial Tenax sample. Hydrogen sulfide, carbonyl sulfide and naphthalene appear to be generated at effectively a constant level after the initial transient. The relatively constant values for hydrogen sulfide and carbonyl sulfide shown in Figure 19 probably result from the gasification of sulfur retained with the char after the devolatilization process is effectively complete. It is believed that the behavior shown by naphthalene results from its being held up in its passsage through the tar trap and sampling system much like retention on a chromatographic column. This belief is supported by the fact that naphthalene is less volatile than the other components shown in Figure 19.

It should be emphasized that the concentration scale (ordinate-axis) on Figure 19 displays logarithms of the concentration values. Thus, the concentrations of these volatile organic constituents were found to undergo extreme variations over the duration of the gasification tests, i.e., up to three orders of magnitude in most cases.

6.2.3 Semivolatile Organic Products

Table 16 presents results obtained by solvent partitioning of various tar products resulting from RTI operations and other coal conversion operations. Samples H-1, B-1, and B-2 were obtained to use in this study for the initial testing of the efficacy of the partitioning procedure. The procedure in its present form eliminates losses due to

TABLE 15. ORGANIC COMPOUNDS ADSORBED FROM PRODUCT GAS STREAM
GAS STREAM CONCENTRATION (µg/1)

Compound \ Run	2 Upstream Tenax	2 Steady-State XAD	4 Upstream Tenax	4 Steady-State XAD	6 Upstream Tenax	6 Steady-State XAD	16 Surge XAD	16 Steady-State XAD	16 Tenax NO. 2	16 Tenax No. 4	16 Tenax No. 6
Benzene	5.4		50		7.7				1,100	60	12.6
Thiophene	2.0		6		1.3				150	2.2	0.8
Toluene	7.6				5.7				125	872	6.9
Xylene*	0.13		0.3		9.9	17.8	78	2.6	>52	4.2	1.0
Phenol	0.3		0.2		1.9	23.7	16	1.4			13.0
Dimethyl Phenol	1.1										
C_2-Alkyl Phenol	0.5		1.3				TR				1.8
Naphthalene	9.8	160	52	1.7	35	49.7	61	15.8	81		83
Biphenyl		14	0.075	0.4		0 4	0.7	0.3			
Anthracene		1.3		0.07		0.0					
Indane			TR			4.4	3.2	0.61	8		1.2

TABLE 15 (cont'd)

Compound \ Run	2 Upstream Tenax	2 Steady-State XAD	4 Upstream Tenax	4 Steady-State XAD	6 Upstream Tenax	6 Steady-State XAD	16 Surge XAD	16 Steady-State XAD	16 Tenax NO. 2	16 Tenax No. 4	16 Tenax No. 6
Methanethiol (Methyl Mercaptan)			0.1								
Cresols*			0.2			68.1	12		43		6.3
Dibenzofuran					(0.07)	(1.6)		0.53			
Fluorene							TR	0.1			
Fluoranthene							2.7	TR			
Pyrene							0.4	TR			
Benzothiophene (+ Dimethylphenol)	2.3							3.7			1.3
Acenaphthene						0.4					

TR = Trace Quantity
NQ = Not Quantitated
* = Includes Isomers
( ) = Tentative Identification

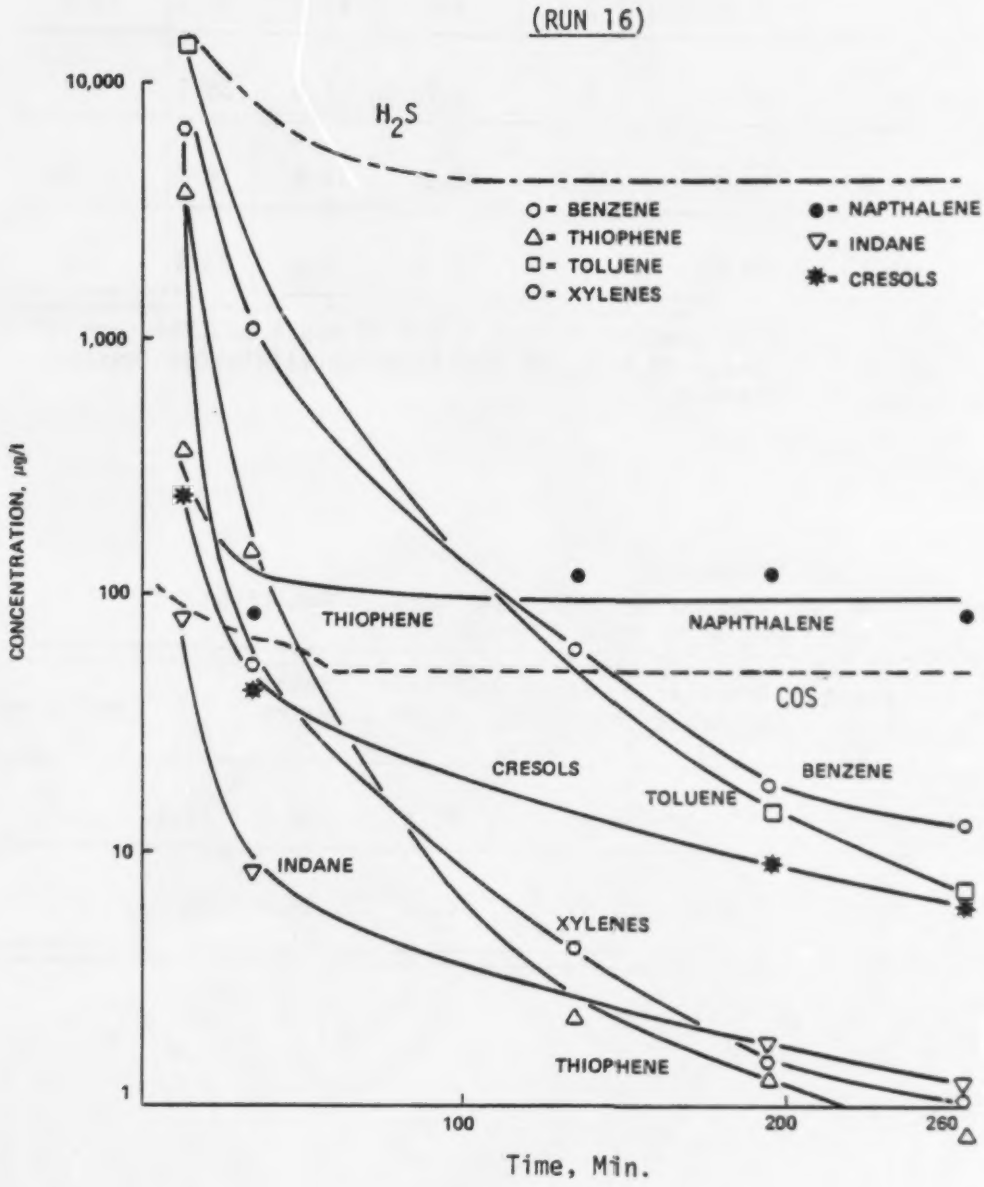


Figure 19. Gas product/contaminants during run 16.

TABLE 16. WEIGHT PERCENT OF VARIOUS TAR FRACTIONS VIA PARTITION PROCEDURE

Sample No. (Source)	Total Tar (g)	Nonpolar Neutrals (%)	Polar Neutrals (%)	Organic Acids (%)	Organic Bases (%)	PNA (%)	Insolubles (%)
H-1	--	3.2	12.1	14.2	1.3	18.3	13.6
B-1	--	7.5	5.6	3.4	41.9	22.8	13.5
B-2	--	20.1	8.6	2.7	1.5	38.9	4.4
Run 6* (RTI)	15.9	13.0	13.8	30.3	12.5	16.5	13.9
Run 16* (RTI)	48.7	29.8	8.1	13.2	6.0	33.3	9.6

*Partition procedure used with samples of Runs 6 and 16 was a modification of that used with sample H-1, B-1, and B-2; the modification eliminated losses due to the existence of emulsions.

TABLE 17. WEIGHT PERCENT RECOVERY VIA MODIFIED PARTITION PROCEDURE WITH MODEL COMPOUNDS

Sample No. (Source)	Sample Mass (g)	Nonpolar Neutrals (%)	Polar Neutrals (%)	Organic Acids (%)	Organic Bases (%)	PNA (%)	Insolubles (%)
CLS-1 (RTI)	0.258	22.2	97.3	92.3	94.8	75.8	--
CLS-2 (RTI)	0.031	80.2	72.0	97.2	96.4	100	--

the existence of emulsions by use of a particular wash sequence. This procedure is displayed in Figure 20 with underlines denoting the modifications (updated steps) that have been introduced to the procedure.

Table 17 displays information on the validation of the modified partitioning procedure. Validation was conducted using model organic compounds. It employed benzoic acid and phenol (organic acids), quinoline (organic base), hexadecane (nonpolar neutral), ethylene glyocol (polar neutral) and phenanthrene (PNA). These results are regarded as quite acceptable with one exception. The 22.2 percent recovery for the hexadecane in Sample No. CLS-1 is regarded as a spurious result. About 97 percent recovery has been achieved for nonpolar substances in subsequent tests.

Three fractions from the partitioning of the tars collected during Run 6 have been analyzed using high resolution capillary column gas chromatography analyses/mass spectrometer detection/computer data processing. Figure 21 and Table 18 present these results for the organic acid fractions. Thirty-one compounds were identified in the organic acid fractions, 17 of which were phenol-type compounds. Section 7.5 of this report discusses the hazard potential of the various organic compounds which have been detected in this study.

Figure 22 and Table 19 present the results of the organic base fractions from the tar material of Run 6. Some 40 compounds have been identified in this fraction, most of which are nitrogen-containing organic compounds representing substituted pyridines, quinolines and carbazoles. The phthalate esters detected in the organic acid and the organic base fractions may well represent artifacts resulting from plasticizers that have been utilized in the manufacture of plastic components of the gas sampling system.

Figure 23 and Table 20 show the output achieved for the polynuclear aromatic (PNA) fraction from the tar collected during Run 6. These compounds range from two to five condensed aromatic ring structures. The

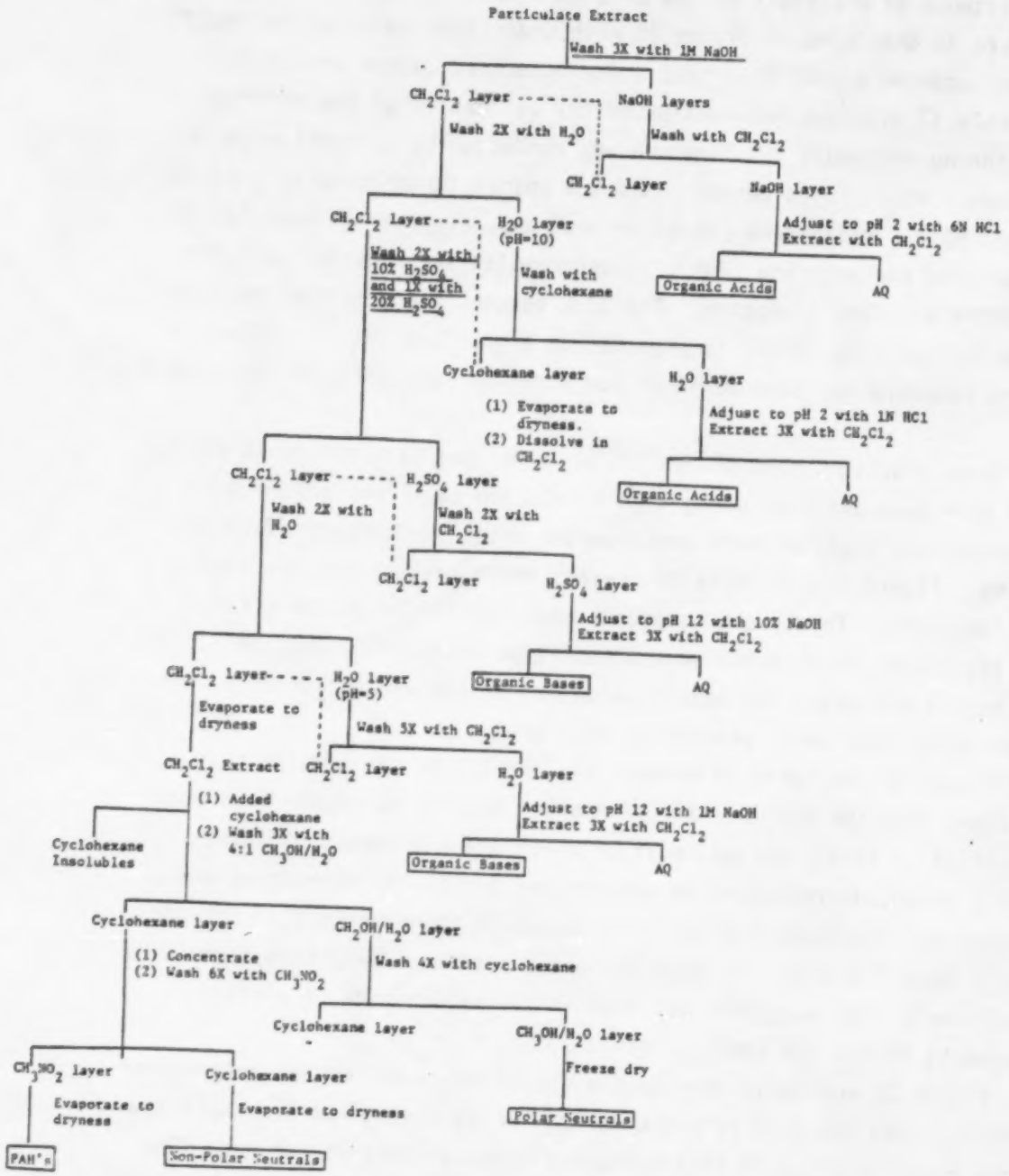


Figure 20. Modified partition scheme for semivolatiles.

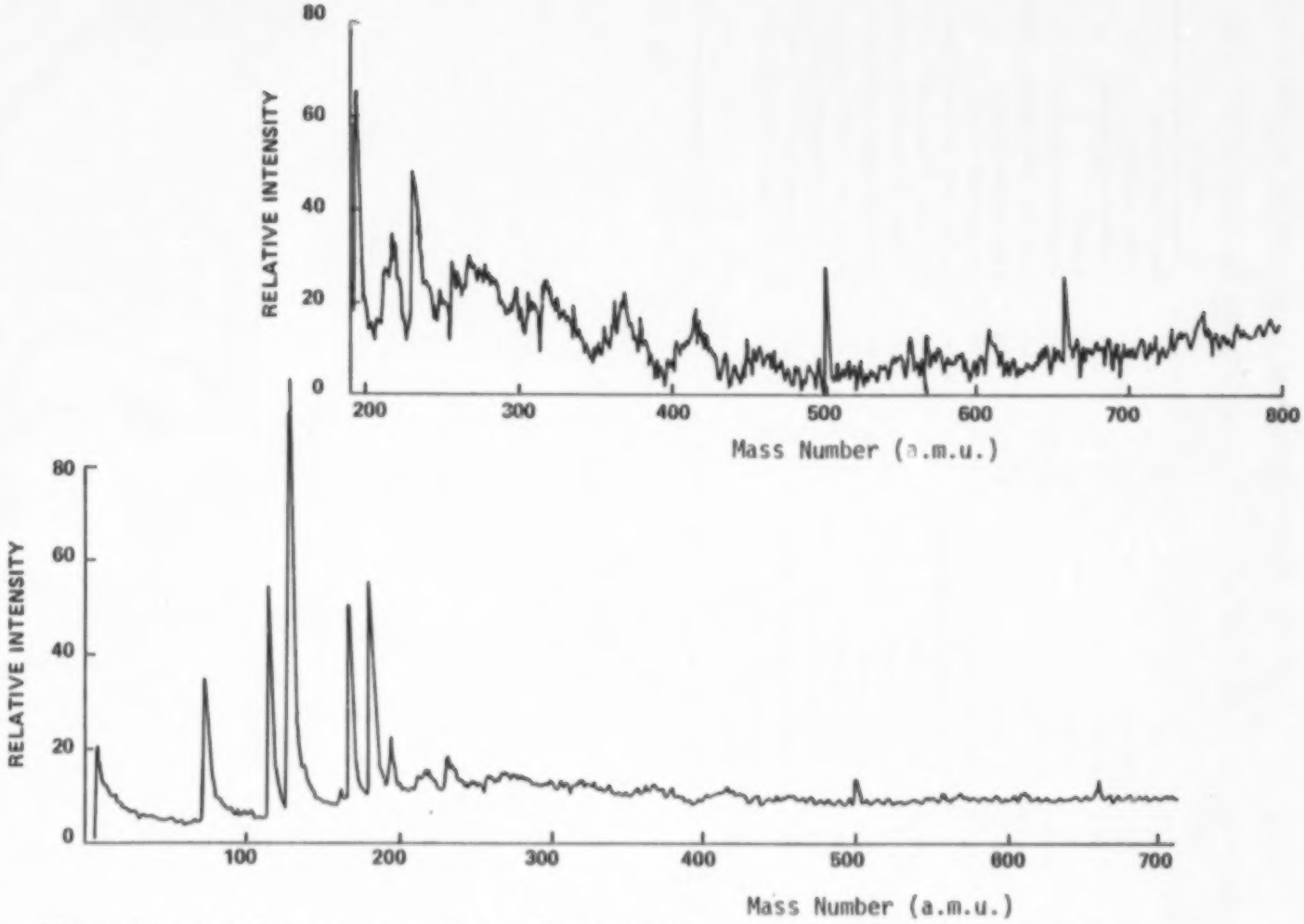


Figure 21. Total ion current plot. Semivolatile organic acid fraction from run 6.

TABLE 18. COMPOUNDS IDENTIFIED IN THE SEMIVOLATILE ORGANIC ACID FRACTION FROM RUN 6

Chromatographic Peak No.	Elution Temp. (°C)	Compound	Chromatographic Peak No.	Elution Temp. (°C)	Compound
1	74	phenol	13	144	p-ethylacetophenone
2	87	o-cresol	14	151	i-butyl cinnamate
3	90	p-cresol	15	160	di-t-butyl-4-ethylphenol
3	91	m-cresol	16	162	β-naphthol
4	94-102	xylenols	16	163	o-nitroso-β-naphthol
5	106-109	ethylphenols	17	167	α-naphthol and phthalates (plasticisers)
6	110	C_2-phenol	18	173	α-methoxynaphthalene
7	115	methylethylphenol	19	178	β-methoxynaphthalene
7	115	o- and m-hydroxyacetophenone	20	189	1,2-dihdro-3,5,8-trimethylnaphthalene
8	121-122	methylethylphenols	21	198	phthalates (plasticiser)
8	122	trimethylphenol	22	201	di-butyl phthalates (plasticiser)
9	129	o-allyl phenol	22	202	dicyclohexylphthalate (plasticiser)
10	129	terephthalaldehyde	23	233	2-n-propyl-5-i-butylthiophene
11	132	7-methylbenzo(b)furan	23	235	4-t-butyl phenoxymethylacetate
11	133	2-methyl-5-phenyltetrazole	23	236	4,9-dimethyl naphthol(2,3-b)thiophene
11	134	vinylphenylcarbazole	24	263	butyl phthalyl butyl glycolate
12	137	phenyl-2-propynyl ether			

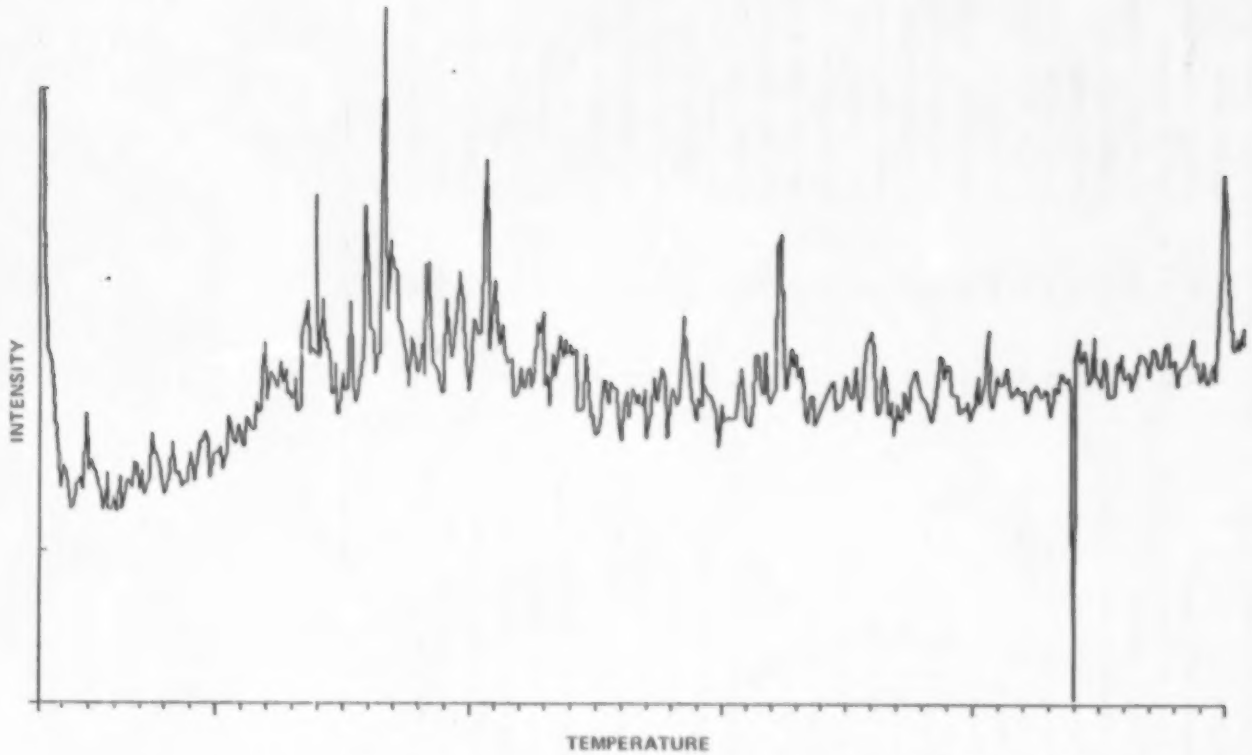


Figure 22. Total ion current plot. Semivolatile organic base fraction from run 6.

TABLE 19. COMPOUNDS IDENTIFIED IN THE ORGANIC BASE FRACTION FROM RUN 6

Chromatographic Peak No.	Elution Temp. (°C)	Compound
1	103	pyridine
2	114	N-methyl-o-toluidine?
3	117	4-acetyl pyridine
4	122	quinoline butiodide
5	126	2,6-dimethyl-4-ethyl pyridine
6	140	6-methyl quinoline
7	140	3- or 4-methyl quinoline
8	141	2-amino-5-chloro-4,6-dimethyl pyrimidine
9	144	8-nor-propyl quinoline
10	145	ethyl quinolines or 2-amino-5-chloro-4,6-dimethyl pyrimidine
11	154	2,6-dimethyl quinoline
11	154	ethyl quinolines
12	154	3,5,5-trimethyl-1-hexanol?
13	156	4-ethyl quinoline
14	157	C_2-quinoline isomer
14	157	3-nor-propyl quinoline
15	160	phenyl-2-pyridone isomer
16	162	phenyl-2-pyridone isomer
16	162	2,6-dimethyl quinoline
17	164	1,2,3,4-tetrahydrocarbazole?
18	166	4- and 6-phenyl-2-pyridone
18	166	ethyl quinoline
19	168	methyl-3-allylindolenine isomer
20	170	4-nor-propyl quinoline
20	170	methyl-allylindoline isomer
21	173	methyl-allylindoline isomer
22	175	methyl-allylindoline isomer
22	175	4-phenyl-2-pyridone
23	178	diphenyl amine
24	179	2-amino-4-phenyl-6-methyl pyrimidine
24	179	phenyl-2-pyridone
25	180	2,2'-dimethyl-4,4'-dipyridyl
26	192	N-methyl carbazole?
27	194	2-methyl carbazole
28	197	benzoquinoline
30	198	acridine or benzoquinoline
30	200	benzoquinoline
30	200	amino-9-ethyl carbazole isomer
31	207	amino-9-ethyl carbazole isomer
32	210	methylbenzoquinoline
33	211	amino-9-ethyl carbazole isomer
34	216	methylbenzoquinoline
35	221	methylphenylindole isomer
36	224	methylphenylindole isomer
37	226	methylbenzoquinoline
38	229	methylphenylindole isomer
39	234	fluoranthene
39	234	methylbenzoquinoline
40	238	4-styrylquinoline?
40	238	methylphenylindole isomer
41	240	3-benzylindene phthalimidine
41	240	methylbenzoquinoline
41	240	methylphenylindole isomer
42	246	4-(1,2,3,4-tetrahydro-2-naphthyl)-morpholine
43	262	3,4-diphenyl pyridine
44	265	dibutyl phthalates (plasticiser)
45	265	di-2-ethylhexylphthalate (plasticiser)

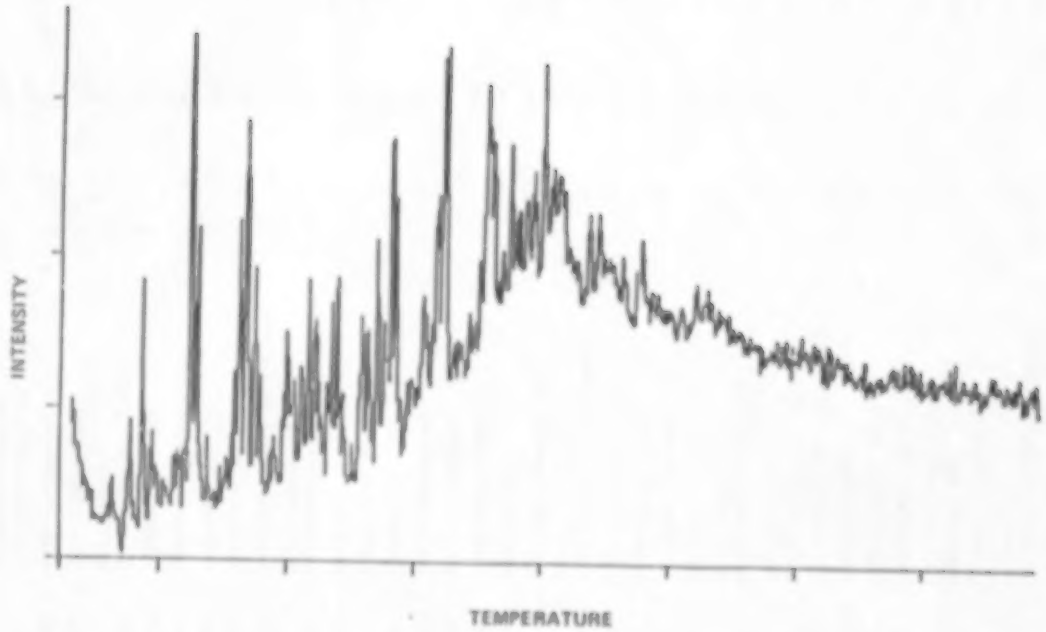


Figure 23. Total ion current plot. Semivolatile PNA fraction from run 6.

TABLE 20. COMPOUNDS IDENTIFIED IN THE SEMIVOLATILE PNA FRACTION FROM RUN 6

Chromatographic Peak No.	Elution Temp. (°C)	Compound
1	117	methyl phenyl acetylene?
2	124	7-methylbenzo(b)furan
3	130	methyl indenes
4	134	naphthalene
4	134	2,3-dihydro-2-methylbenzofuran
5	137	1-hydroxy-2-methyl-4-ethyl-benzene
5	137	hydroxyacetophenone?
6	139	1-methyl-4-nor-hexyl-1,2,3,4-tetrahydronaphthalene
7	150	2-methylnaphthalene
8	153	1-methylnaphthalene
9	165	ethylnaphthalene
9	165	2,6-dimethylbenzo(b)thiophene
10	166	1,3-2,6-2,7-, and 1,6-di-methylnaphthalene
11	169	1,3- and 2,3-dimethyl-naphthalene
12	172	1,3-dimethylnaphthalene
13	174	1,2-dimethylnaphthalene
14	178	acenaphthene or biphenyl
14	178	methylbiphenyl
15	181	2-ethyl-5(or 7)-methylbenzo(b) thiophene
15	181	2-i-propylnaphthalene
16	182	dibenzofuran
17	184	propylnaphthalene
18	186	propylnaphthalene
19	187	propylnaphthalene
20	190	fluorene
20	190	propylnaphthalene
21	192	fluorene
22	193	1,3-dihydro-4,6-dimethylthieno (3,4-c)thiophene
23	194	2-methylbiphenyl or fluorene
24	198	2-hydroxyfluorene
24	198	fluorene
25	198	2-tert-butylnaphthalene
26	199	2-hydroxyfluorene
27	202	1-methyl-7-iso-propyl-naphthalene?
28	210	1-methylfluorene
29	213	methoxyfluorenes
30	215	methoxyfluorenes or ortho- and para-phenylanisole
31	218	phenanthrene
31	219	anthracene
32	224	dimethylfluorene
33	230	3-methyldibenzothiophene
34	231	phenyl M-xylyl ketone?
34	231	methyldibenzothiophene
35	234	methyldibenzothiophene
35	236	methylphenanthrene
36	239	N-methylcarbazole
36	239	methylcarbazole isomer
37	240	methylcarbazole isomer
38	242	tetrahydroanthraquinone?
39	244	4,5-dimethyl-9,10-dihydro-phenanthrene?
40	252	dimethylphenanthrene
40	252	pyrene
41	253	pyrene
42	255	8-nor-butyl-phenanthrene?
43	256	ethylanthracene
44	258	pyrene
45	261	1-methylbenzo(1,2-b:4,3-b)-dithiophene
46	263	hexadecapyrene?
47	264	trimethylphenanthrene?
48	265	1-methylpyrene
49	265	trimethylphenanthrene
49	265	methylpyrene
50	265	methylpyrene
50	265	trimethylphenanthrene
50	265	1,4-dimethylanthracene
51	265	1,2,3,4-tetrahydrotriphenylene
51	265	1,4-dihydro-2,3-benzcarbazole
52	265	tetrahydrotriphenylene
52	265	dihydrobenzcarbazole
52	265	methylpyrene
52	265	4,4'-dichlorobiphenyl?
53	265	tetrahydrotriphenylene
53	265	methylpyrene
53	265	dihydroxyanthraquinone
54	265	butyl phthalyl butyl phthalate (plasticiser)
54	265	3-nor-hexylperylene?
54	265	3,6-dimethoxyphenanthrene
55	265	3,3'-Bi-indolyl
55	265	4,4'-dichlorobiphenyl
56	265	1,2-diphenylbenzene
57	265	1,4-diphenylbenzene
58	265	1,3-diphenylbenzene

Table 20 (cont'd)

Chromatographic Peak No.	Elution Temp. (°C)	Compound	Chromatographic Peak No.	Elution Temp. (°C)	Compound
59	263	tetrahydrobenzo(a)anthracene	64	263	3-methylbenzo(a)anthracene?
60	263	diphenylbenzoate	65	263	9-, 10-, or 11-methylbenz(a)-anthracene
61	263	triphenylene			
62	263	di-sec-octylphthalate (plasticizer)	66	263	perylene? or benzpyrene?
62	263	di-2-ethylhexylphthalate (plasticizer)	67	263	5,9-dimethylbenzo(c)phenanthrene?
			67	263	benzpyrene or perylene
63	263	methylbenzo(a)anthracene or 3-methylchrysene or 2-methyltriphenylene	68	263	3-methylacenaphthylene

two-ring compounds are represented by benzofuran, methyl indene or naphthalene. Five-ring structures are benzopyrene or perylene.

The tar product from Illinois No.6 coal obtained in Run 16 has been analyzed to yield results shown in Table 21. These compositions expressed in percent by weight are compared to those obtained with tar from the Morgantown Energy Research Center (MERC) fixed-bed coal gasification unit. These results indicate that a wide variety of complex organic compounds is present in the coal gasifier tar product. This same conclusion is supported by results that were obtained utilizing low ionizing voltages with a direct probe mass spectrometer with these tar products from Illinois No.6 coal. The direct probe mass spectrometer results are summarized as follows:

1. Tar acids -- about 50 significant peaks at 300 to 500 amu, 50 minor peaks at 350 to 400 amu, and few peaks beyond about 420 amu (190°C).
2. Tar bases -- major components at 200 to 350 amu, about 70 minor components at 400 to 470 amu, and few peaks beyond 470 amu (235°C).
3. Nonpolar neutrals -- significant peaks up to 450 amu (230°C).
4. Polar neutrals -- major components at 200 to 400 amu, about 60 minor components from 540 to 620 amu, and few peaks beyond about 630 amu (230°C).
5. Polynuclear aromatics -- major peaks at 178 to 350 amu in increments of 24 to 26 amu, and few peaks beyond 380 amu.

TABLE 21. QUANTITATION FOR SEMIVOLATILE ORGANIC COMPOUNDS IN COAL GASIFIER TAR PRODUCT

Compound	RTI Illinois No.6 Coal (%)	MERC[11] Pittsburgh Coal (%)
Naphthalene	1.97	3.00
Anthracene	1.31	NA
Fluoranthene	0.71	0.01
Phenanthrene	0.41	0.55
Benzidine	0.36	NA
Pyrene	0.21	NA
m-Cresol	0.04	1.20
Phenol	0.03	0.62
o-Cresol	0.02	0.57
Fluorene	0.01	1.19
Dibenzofuran	0.001	1.14

7.0 DISCUSSION OF RESULTS

The results which have been obtained in preliminary tests deal with the performance of the coal gasification reactor process, the degree of conversion of coal and coal char feed material and the initial characterization and quantitation of the chemical constituents of the primary gaseous product stream, the volatile organic products and the semivolatile organic materials. The gasification reactor system, the signal processing and control system, the product sampling system and the chemical analysis procedures have all been developed, tested and implemented. A full program of testing and study of pollutant formation has started on a variety of solid feed material using various selected operating conditions.

7.1 FEED CONVERSION

The gasification studies that have been conducted to date utilized either a char from Western Kentucky coal or raw Illinois No.6 coal. These runs were conducted at a pressure of 1.5 MPa (200 psig). Steam was fed to the conversion reactor in all the runs whereas only runs designated as combustion heat runs used an air feed stream. The external vertical furnace on the reactor was operated during each run so as to achieve a predetermined temperature vs. time history for the reaction process. The operability of the reactor system was thus demonstrated for achieving desired operating conditions.

As the bed temperature increased, the relative proportion of hydrogen in the effluent gas from char gasification was found to dramatically increase. This indicates that as the bed temperature increases, hydrogen is produced by the reaction of steam with the char material. Both the char/steam and the char/oxygen reactions are known to have a substantial temperature dependence. These reactions are discussed in Appendix I of this report. Reaction rates, in general, increase with temperature. For the conditions experienced to date, the rates of feed

conversion have been more than twice as great in the combustion heat runs compared to the runs in which no air or oxygen was fed to the reactor.

Gasification of Illinois No.6 coal in the RTI reactor initially involves the devolatilization of the coal. Dramatic changes are seen during the early periods of these runs regarding the volatile matter content of the coal as well as the sulfur content (cf., Tables 2-6). Primary gas stream compositions similarly indicate that initial devolatilization takes place and results in a high level of methane formation in the reactor (cf., Figures 7-9).

Sufficiently complete information is available on Runs 2, 4, 6 and 16 of the runs completed to date to provide insight as to the influence of the steam and air rates on the gasification process. The air-to-steam mass ratios were 1.0 and 0.5 for Runs 2 and 16, respectively. No air was used for Runs 4 and 6. Hence, Runs 2 and 16 are designated as combustion heat test runs and Runs 4 and 6 are regarded as external heat test runs. A comparison of Runs 6 and 16 indicates that the level of sulfur conversion was effectively the same for these two runs, i.e., about 90 percent. Yet, more feed material and a higher carbon content of that material was consumed in Run 16 over essentially the same time period. In particular, the gasification rate for Run 16 was approximately 42 kg/hr m^2 as compared with 20 kg/hr m^2 for Run 6.

Generally, the coal gasification reactor and its accessories have been demonstrated to be able to simulate operating conditions characteristic of those prevailing in commercial and/or developmental gasification reactors. Operating conditions and primary gas stream compositions have been tabulated for use in the selection of operating conditions for the test runs (cf., Tables 7 and 8). Reactor operating parameters for future test runs will be varied in order to study the influence of the reaction operating conditions upon the nature and concentration of the various pollutants which result from the process. Parameters will include air-to-steam mass ratios up to about 10.0, pressures to 2.3 MPa (300 psig) and various operating temperatures in order to encompass the range of operating conditions of practical significance.

The tests conducted to date have been in the fixed bed reactor configuration. Lurgi coal gasifiers[26,27,30] in commercial use are of this type. Fixed bed reactors for use with U.S. coals have been under development for a number of years.[2,7,14,31] Hence, it is clear that the fixed bed configuration is an important one for investigation. In addition, it is anticipated that experimental studies in a fluidized bed configuration will be feasible as a part of the current project. Fluidized bed coal gasifiers and combustion units are also under active development in this country. A leading example is the Synthane process system[9,16,25] at the Pittsburgh Energy Research Center.

7.2 PRIMARY GASEOUS PRODUCTS

There are six primary gas products with concentrations generally in the 1 percent by volume level or greater. These are nitrogen, hydrogen, carbon monoxide, carbon dioxide, methane and hydrogen sulfide. Steam is also present in the product gas stream. However, condensation occurs within the tar trap and the gases are dried prior to chemical analysis. Gas composition values are expressed on a moisture-free basis.

As was anticipated, the composition of the effluent gas stream varies appreciably with changes in the type of feed material as well as changes in the feed rates of steam and air. In addition, the operating temperature has been found to influence the composition of the product gas stream (cf., Tables 4-6 and Figures 7-12). Generally, it is known that steam is consumed by both the carbon/steam reaction and the water-gas shift reaction. These reactions produce hydrogen, carbon monoxide and carbon dioxide. Based on the methane levels obtained in the runs reported herein, it is clear that some of the hydrogen reacts with the carbon to produce methane. The carbon-hydrogen reaction may in fact be the predominant mode of methane formation after the initial devolatilization period.

The amount of gas product resulting from the gasification of a unit weight of feed material was found to be 2.7 to 2.9 Nm^3/kg for each of the coal runs. With char feed material, however, the measured rates of effluent gas per unit weight of char converted were higher since more

reactant gas passed through the reactor per unit of feed material converted (cf., Table 7).

7.3 VOLATILE ORGANIC PRODUCTS

High levels of ethane, ethylene, carbonyl sulfide, methyl mercaptan and thiophene were measured during the devolatilization process for the runs involving Illinois No.6 coal (cf., Tables 4-6 and Figures 10-12). Ethane and hydrogen sulfide concentrations as high as 3.85 and 3.45 percent, respectively, were detected after 45 minutes of reactor operation in Run 6. These values dropped off to steady-state levels of approximately 5000 ppm and 20 ppm for the hydrogen sulfide and ethane, respectively. Propane and propylene were also detected in the ppm concentration range as products of the devolatilization process. The behavior of those constituents associated with devolatilization was found to be quite distinct from those associated with the char gasification process. The devolatilization products were found to reach maximum values quite rapidly or to be at high levels initially and then decay quite rapidly to very low levels. This was characteristic of ethane, ethylene, propane, propylene, methyl mercaptan and thiophene. Alternatively, hydrogen sulfide and carbonyl sulfide reached effectively level values for extended periods of time, i.e., four hours and beyond.

In addition to the volatile organic constituents of the primary gas streams that were analyzed via direct gas chromatographic techniques, other volatile organic compounds were present at low levels and/or possessed somewhat higher boiling points. They were removed from the gas stream using either Tenax or XAD-2 adsorbent cartridges. The Tenax was found to be most effective for adsorbing polar compounds such as alcohols, glycols, diols, phenols, amines, amides, aldehydes and ketones. Further, it was effectively desorbed upon heating. The XAD-2 adsorbent was found to be particularly effective for aromatic hydrocarbons, which can form pi:pi bond complexes with its structure. Organic compounds were removed from the XAD-2 material via Soxlet extraction using methylene chloride. The procedure for sample collection and sample retrieval from these adsorbents has been validated for use in this project.

Numerous compounds were found in the products of the gasification tests at concentrations at the microgram/liter level (cf., Figures 13-18). The Tenax cartridge samples collected from the gasification of char showed prominent peaks that have been interpreted as benzene, toluene, thiophene, phenol and naphthalene. The gasification tests with Illinois No.6 coal yielded additional prominent peaks from the sample collected via the Tenax adsorbent material. These peaks represented primarily benzene, thiophene, methyl thiophene, phenol, cresols, alkyl-substituted benzenes, benzofuran, methyl-substituted benzofuran and naphthalene.

The XAD-2 resin was more effective for removing compounds having boiling points just above benzene, i.e., toluene, phenol, thiophene, derivatives, indene, cresols, naphthalene, etc. This resin therefore, is particularly effective in accumulating the organic compounds that are present in lower concentrations and are less volatile (cf., Figures 16 and 18).

A quantitative determination of concentrations of compounds of interest used both internal and primary standard samples with the mass spectrometer system. For the Illinois No.6 coal used in Run 6, the prominent peaks resulting from the XAD-2 resin were xylenes, phenol, indan, indene, cresols, methyl indene and naphthalene. The concentrations of the phenol, indan and naphthalene were 23.7, 4.4, and 49.7 mg/m^3, respectively. Additional PNA compounds identified in the sample at 0.1 mg/m^3 or greater were β-methyl naphthalene, biphenyl, acenaphthalene and anthracene. Section 7.5 of this report deals with the potential hazard associated with these compounds.

7.4 SEMIVOLATILE ORGANIC PRODUCTS

The organic compounds that were collected in the tar trap are referred to as semivolatile organic compounds since these materials have very high boiling temperatures. Water also condenses in this trap. Thus, organic compounds in the effluent stream possessing a relatively high water solubility accumulate to some degree in this trap. They include

phenol and cresols. The partitioning scheme developed for use in this project has been validated relative to its capability for separating the tar produced into the categories of organic acids, organic bases, polar neutral compounds, nonpolar neutral compounds, PNA hydrocarbons and cyclohexane insoluble material.

Various analytical methods have been studied for use in the analysis of the fractions resulting from partitioning of the tars. The methods include exclusion chromatography, reverse phase chromatography, nuclear magnetic resonance analysis and direct probe mass spectrometry. The greatest success has been achieved utilizing capillary chromatography columns with temperature programming and GC/MS detection for these semivolatile compounds. The use of low ionizing voltages with a direct probe mass spectrometer has made it possible to detect the parent compounds for these semivolatile organic materials.

The primary results obtained to date for the chemical analysis of the organic acids, organic bases and PNA compounds have been achieved using high resolution capillary column gas chromatographic analysis/mass spectrometer detection/computer data processes (cf., Figures 21-23 and Tables 18-20). Almost without exception, the organic acids were found to be oxygen-containing compounds. These include phenols, furans, ethers, etc. The organic bases were primarily nitrogen-containing compounds including derivatives of pyridine, quinoline, carbazole, diphenyl amine and other compounds. The PNA fractions showed condensed ring aromatic structures from two to five rings as the predominant material. These include naphthalene, fluorene, phenanthrene, anthracene, pyrene, methyl pyrene, triphenylene, and benzpyrene. A few compounds containing hetero-atoms were also detected in the PNA fractions. Some of these were derivatives of benzofuran, hydroxyfluorene, methyl carbazole, etc. The following section of this report discusses the potential hazards associated with many of these compounds.

7.5 EVALUATION OF RESULTS

This report on pollutant production from synthetic fuels has involved equipment construction, installation and preliminary testing. The results that have been obtained to date on the gasification of char and coal are for a relatively narrow range of operating conditions. The initial emphasis has been placed upon achieving the successful operation of the reactor and sampling system as well as the reliable chemical analysis of the various compounds generated in the gasification process. The gasification tests have been conducted at high steam partial pressures and low or zero air flow rates. In all cases, external heat has been applied to the reactor utilizing the vertical reactor furnace. Carbon conversions have been carried to about 88 percent for some 2 kg of coal during the most exhaustive tests to date.

Preliminary evaluation has been made of the chemical analysis results obtained for the gasification of char and raw coal. The results show that very high levels of volatile and semivolatile organic compounds are produced during the initial period of the gasification run from the volatile matter content of the raw coal. This material is made up of many compounds and probably possesses a high hazard potential.[10,13] The tests which have been conducted with and without air flow indicate that the presence of air generally tends to result in more internal heat generation within the coal bed and subsequently higher local temperatures within the bed. Higher levels of carbon monoxide on a nitrogen-free basis were measured for those runs for which air was provided as one of the feed streams, whether the primary reactant was char or raw coal.

The amount of tar material produced in the runs with raw coal was quite substantial, i.e., of the order of 0.022 kg of tar/kg of coal converted (40 lbs of tar/ton of coal converted). The amount of gas products formed/unit of coal converted was also substantial, some 2.8 Nm^3/kg (45 scf/lb). These results for the tar and gas produced during the RTI laboratory gasification tests with Illinois No.6 coal have been found to be in very close agreement with results which have been obtained

with this same coal on the fixed bed gasifier at the Morgantown Energy Research Center.[2,11,14,15] Comparable values have been achieved with other commercial and/or developmental gasification processes[7,15,21,31] (cf., Tables 7 and 8).

A list of 102 specific hazardous compounds that have been selected for identification in this work is presented in Table 22. The compounds listed in this table are either on the EPA Effluent Guidelines Division's list of primary pollutants for BAT revision studies (consent decree compounds), possess minimum acute toxic effluents (MATE) values which are $\leq$ 17 mg/m^3 or are known to be associated with coal conversion processes in relatively high concentrations. The MATE value of 17 mg/m^3 or less has been established in order that only compounds having a high hazard potential will be included, yet the list of compounds so selected would be of manageable proportion. This criterion also represents a concentration level at which measurements can successfully be made utilizing the chemical analysis techniques which have been selected for use in this study. See Appendix II for a presentation of background concepts on the use of MATE and EPC values as "multimedia environmental goals."

Indication is provided in Table 22 as to which of the listed compounds are on the consent decree list, which have been identified in the effluents from the laboratory gasifier runs conducted to date and which have been identified in effluents from other coal conversion operations. In the latter category are those compounds which have been found in the effluent stream from the fixed bed pilot gasifier at the Morgantown Energy Research Center[23] and those which have been reported in the effluent from coal liquefaction operations[24,25] as well as those from coal coking operations.[3]

Of the 102 specific hazardous compounds listed, 42 are consent decree compounds. A total of 25 hazardous compounds have been identified in the effluent stream from the RTI gasifier, 21 have been identified in effluents from the MERC gasifier, 39 in the products of various coal liquefaction operations and 52 in the products of coal coking operations. Some 33 of the 102 compounds on the list are PNA materials. Of these 33, 14 have been detected in the effluents from the RTI laboratory gasifier to date.

TABLE 22. LIST OF SPECIFIC HAZARDOUS COMPOUNDS FOR IDENTIFICATION IN THIS STUDY

MEG's No.	Consent Decree Compounds	Name	Type	I RTI	II MERC	III Coal Liq.	IV Coal Coking
02A020	*	Methyl Bromide	PN				
02A040	*	Methyl Chloride	PN				
02A080	*	Methylene Chloride	PN				
02A250	*	Chloroethane	PN				
02B020	*	Vinyl Chloride	PN				
03B060		1,4-Dioxane	NN				
04A020		Chloromethyl Methyl Ether	PN				
05B100		1-Phenyl Ethanol	PN				
07A020		Formaldehyde	PN			X	X
07A060	*	Acrolein	PN				
07B080	*	Isophorone	PN				
08A160		Phthalic Acid	TA				
08B060		3-Hydroxypropanic Acid	TA				
08B100		β-Propiolactone	PN				
08D280	*	Phthalate Esters	PN	X			
09A040	*	Acrylonitrile	TB				
09A060		1-Cyanoethane	PN				
10A040		Ethyleneimine	TB				
10A060		Ethanolamine	TB				
10A140		Butylamines	TB				
10C040		Aminotoluenes	TB				X
10C080		Anisidines	TB				
10C100		1,4-Diaminobenzene	TB				
10C120		4-Aminobiphenyl	TB				
10C140	*	Benzidine	TB				
10C200		1-Aminonaphthalene	TB				X
10C220		2-Aminonaphthalene	TB				X
11A020		Diazomethane	TB				
11B020		Monomethylhydrazine	TB				
11B080	*	1,2-Diphenylhydrazine	TB				

continued

TABLE 22. LIST OF SPECIFIC HAZARDOUS COMPOUNDS FOR IDENTIFICATION IN THIS STUDY (continued)

MEG's No.	Consent Decree Compounds	Name	Type	I RTI	II MERC	III Coal Liq.	IV Coal Coking
12B020		N-Methyl-N-Nitroso-Aniline	TB				
13A020		Methylmercaptan	PN	X		X	X
13A040		Ethanethiol	PN	X			X
13A080		n-Butanethiol	PN				
13A100		Benzenethiol	PN				X
14B020		Dimethyl Sulfoxide	PN				
15A020	*	Benzene	PNA	X	X	X	X
15A040	*	Toluene	PNA	X	X	X	X
15A060	*	Ethyl Benzene	PNA	X	X	X	X
15A160		Biphenyl	PNA	X	X	X	X
15B020		Indane	PNA	X	X	X	X
15B080		Xylene	PNA	X	X	X	X
16A020	*	Chlorobenzene	PN				
16A202	*	2-Chloronaphthalene	PNA				
16B020		α-Chlorotoluene	PNA				
17A020	*	Nitrobenzene	PN				
17A060		4-Nitrobiphenyl	PN				
18A020	*	Phenol	TA	X	X	X	X
18A041		Cresol	TA	X	X	X	X
18A042		m-Cresol	TA	X	X	X	X
18A140		Xylenols	TA	X	X	X	X
18A142	*	2,4-Xylenol	TA				
18A144		2,6-Xylenol	TA			X	X
18B060		1,4-Dihydroxybenzene	TA				X
19A020	*	2-Chlorophenol	TA				
19A040	*	2,4-Dichlorophenol	TA				
20A020	*	2-Nitrophenol	TA				
20A040		3-Nitrophenol	TA				
20A060	*	4-Nitrophenol	TA				
20A100	*	2,4-Dinitrophenol	TA				

continued

TABLE 22. LIST OF SPECIFIC HAZARDOUS COMPOUNDS FOR IDENTIFICATION IN THIS STUDY (continued)

MEG's No.	Consent Decree Compounds	Name	Type	I RTI	II MERC	III Coal Liq.	IV Coal Coking
21A020	*	Naphthalene	PNA	X	X	X	X
21A100	*	Acenaphthene	PNA	X	X	X	X
21A120	*	Acenaphthylene	PNA			X	X
21A140	*	Anthracene	PNA	X	X	X	X
21A180	*	Phenanthrene	PNA		X	X	X
21B040	*	Benz(a)anthracene	PNA			X	X
21B060		7,12-Dimethylbenz(a)anthracene	PNA				X
21B080		3-Methylcholanthrene	PNA			X	
21B101		Benzo(c)phenanthrene	PNA				
21B120	*	Chrysene	PNA			X	X
21B180	*	Pyrene	PNA	X		X	X
21C080	*	Dibenz(a,h)anthracene	PNA				X
21C100	*	Benzo(a)pyrene	PNA			X	X
21C160		Picene	PNA				X
21D020		Dibenzo(a,h)pyrene	PNA				X
21D040		Dibenzo(a,i)pyrene	PNA				X
21D080	*	Benzo(ghi)perylene	PNA				X
22A020	*	Fluorene	PNA	X	X	X	X
22B040	*	Fluoranthene	PNA	X	X	X	X
22C020	*	Benzo(k)fluoranthene	PNA			X	X
22C040		Benzo(j)fluoranthene	PNA			X	X
22C080	*	Benzo(b)fluoranthene	PNA				X
23A020		Pyridine	TB	X		X	X
23B020		Quinoline	TB			X	X
23B220		Dibenz(a,j)acridine	TB			X	X
23B240		Dibenz(a,h)acridine	TB			X	X
23C020		Pyrrole	TB				X
23C160		Dibenzo(c,g)carbazole	TB			X	X
23C180		Dibenzo(a,g)carbazole	TB			X	X
23D020		Benzothiazole	TB				
24B020		Dibenzofuran	PNA	X	X	X	X
25A020		Thiophene	PNA	X	X	X	X

continued

TABLE 22. LIST OF SPECIFIC HAZARDOUS COMPOUNDS FOR IDENTIFICATION IN THIS STUDY (continued)

MEG's No.	Consent Decree Compounds	Name	Type	I RTI	II MERC	III Coal Liq.	IV Coal Coking
25B080		Benzonaphthothiophene	PNA			X	X
42B100	*	Carbon Monoxide	PN	X	X	X	X
45B100		Organotin	Organometals				
46B900		Tetramethyllead	Organometals				
46B920		Tetraethyllead	Organometals				
47A360	*	Cyanides	PN	X	X	X	X
47B160	*	Ammonia	NN	X	X	X	X
76B900		Nickelocene	Organometals				
78B900		Copper-8-Hydroxy-quinoline	Organometals				
83B900		Alkyl Mercury	Organometals				

NN = Nonpolar neutral compounds.
PN = Polar-neutral compounds.
TA = Organic acidic compounds.
TB = Organic basic compounds.
PNA = Polynuclear aromatic compounds.
I = Compound(s) identified in products of coal gasification in this study.
II = Compound(s) identified in products of MERC fixed-bed coal gasifier.
III = Compound(s) identified in products of coal liquefaction experiments.
IV = Compounds identified in products of coal carbonization (coking-operations).

The chemical nature of essentially all of the compounds which have been detected in coal conversion operations is judged to be consistent with the basic chemical nature of the starting material. There are two exceptions to this in Table 22. First, phthalate esters were detected in the RTI laboratory gasifier. This material may be an artifact, i.e., a result of plasticizer which was present in the plastic components of the fittings utilized in the gas sampling system. Second, 3-methyl cholanthrene is reported to have been detected in coal liquefaction operations. This compound typically occurs environmentally via the pyrolysis of cholesterol.

Since the operating temperatures, pressures, and feed materials for coal gasification processes encompass the range of variables typical for many coal liquefaction and/or coal coking processes, it is likely that any of the compounds which have previously been identifed in coal liquefaction or coal coking operations may at some time be identified in a product of a coal gasification process. The work plan for this project should allow clear delineation of those operating conditions under which various compounds are formed as well as the concentrations of these compounds in the effluent stream. Such information is essential to a full and complete evaluation of the occupational health and safety as well as the environmental hazard potential of coal gasification processes.

An initial effort to identify and analyze the environmental hazard represented by the effluent stream of RTI's coal gasification reactor has been performed utilizing the preliminary data resulting from the runs which have been conducted on Illinois No.6 coal. These results are presented in Table 23. The maximum concentration measured for various hazardous compounds is tabulated. Values detected for the gas stream as well as concentrations measured in the aqueous condensate are presented. Those concentration values which exceed their corresponding MATE values are identified with an asterisk. The table also contains the MATE values and Estimated Permissible Concentrations (EPC) for comparison. A MATE value is the estimated concentration of a contaminant in air (or water) which will not result in adverse effects to human health provided

TABLE 23. GASIFIER POLLUTANTS COMPARED TO MINIMUM ACUTE TOXICITY EFFLUENT LIMITS AND ESTIMATED PERMISSIBLE CONCENTRATIONS[5]

Compound	Maximum Concentration Recorded		MATE		EPC	
	gas $\mu g/m^3$	water $\mu g/\ell$	air $\mu g/m^3$	water $\mu g/\ell$	air $\mu g/m^3$	water $\mu g/\ell$
Naphthalene	3.9E5*	5.5E5	5.0E4	7.5E5	119	690
Biphenyl	1.4E4*		1.0E3		2.4	
Anthracene	2.1E3*	3.7E5	5.7E4	8.4E5	133	2000
Benzene	1.1E6		3.0E3	4.5E4	71.4	414
Thiophene	3.8E3		4.5E3	6.7E4	8	40
Carbonyl Sulfide	4.5E2		4.5E5		800	
Hydrogen Sulfide	1.3E8*		1.5E4		364	
Methyl Mercaptan	9.0E5*		1.1E3		2.1	
Toluene	1.4E7*		3.7E5		893	
Xylenes	6.8E5*		4.35E5		1040	
Phenol	2.4E4*	2.0E5*	1.9E4	5.0E0	45	260
Cresols	2.5E5*	3.4E5*	2.2E4	5.0E0	52	304
Fluorene	1.0E2	3.1E3				
Fluoranthene	2.7E3	2.0E5	9.0E4	1.4E6	162	800
Pyrene	4.0E2	5.8E3	2.3E5	0.45E6	556	8333
Phenanthrene		1.1E5*	1.6E3	2.4E4	57	280
Benzidene		1.0E5	1.4E4	2.1E5	25	124
Dibenzofuran	1.6E3	3.1E2				
Benzothiophene	8.E3		2.3E4		41	
Acenaphthene	4.8E2					

*Value listed exceeds corresponding MATE value.
MATE = minimum acute toxicity effluent limit value.
EPC= estimated permissible concentration value.

exposure is of limited duration. Such a value may represent the upper limit to the acceptable concentration of that substance for an individual pollutant source. The EPC is the estimated concentration of a substance that will not result in toxic effects to humans or to the ecology for continuous exposure. Such values are appropriate for use for ambient air (or water) into which one or many pollution sources have been dispersed. (See also Appendix II.)

As can be seen in Table 23, nine organic compounds were present in the gasifier effluent stream in sufficiently high concentration to exceed the appropriate MATE values for air contamination and three compounds were present in sufficiently high concentrations in the aqueous condensate collected during the run to exceed the appropriate MATE value for water contamination. Hydrogen sulfide, methyl mercaptan, benzene and toluene were the most prominent compounds exceeding their MATE values in the gas phase. Phenol, cresols and phenanthrene were the three compounds exceeding their MATE values for water.

It may be noted that the presence of compounds in the reactor effluent stream at concentrations which exceed the corresponding MATE values does not imply the release of these compounds at the same concentrations. Once the various hazardous materials have been identified and characterized, it should then be possible to design suitable control systems for the removal of these materials. This provides justification for this comprehensive study which aims to identify and characterize the potentially hazardous compounds associated with synthetic fuels production from solid materials.

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APPENDIX I

The Kinetics of Char Gasification

APPENDIX I

THE KINETICS OF CHAR GASIFICATION

The gasification of coal char with steam, or with steam and air, is a much slower process than that of coal devolatilization. Hence, the char conversion rates are of primary importance in determining the overall rate of gasification processes which aim to achieve high levels of carbon conversion. Generally, the char-steam reaction is slower than the char-oxygen reaction, although the activation energy (temperature dependence) is of the order of 35 kilocalories per gram-mole (146 kJ/mol) for both.

The theoretical order of these reactions is not firmly established since the mechanisms for them are not fully understood. It appears that the physical state of the char and the presence of foreign matter can influence the reaction process. In fact, a catalytic effect due to alkali metal compounds is well known. At high steam partial pressures, the char-steam reaction tends toward a zero-order reaction with respect to the steam partial pressure according to experimental evidence. Otherwise, both the char-steam and the char-oxygen reactions, for most practical purposes, can be regarded as first-order with respect to the gas reactant concentration or partial pressure.

The char-steam reaction has been represented with some success by the expression

$$\frac{dx}{dt} = \frac{k_v}{RT}\left[P_{H_2O} - \frac{P_{H_2O}P_{CO}}{K}\,RT\right](1-x).$$

This rate equation accounts for both the forward reaction of char with steam and the reverse tendency of hydrogen and carbon monoxide combination to generate the original reactants. The initial (maximum) rate is

obtained when the second term is deleted, i.e., by the following relation

$$\frac{dx}{dt} = \frac{k_v}{RT} p_{H_2O}(1-x).$$

An examination of rate data published on the char-steam reaction indicates a decided variation of rates with the type of char and the operating pressure. An interpolation of these data[12] for the conditions of this study, viz., high volatile coal char and a pressure of 1.5 MPa (200 psig), give rise to the following rate values:

$$k_v = A_o \exp(-\Delta E_a/RT)$$

where: $\Delta E_a = 37.2$ kcal/mol

$A_o = 5.54 \times 10^3$ $sec^{-1}MPa^{-1}$.

For the char-oxygen reaction, the reacting region is confined to a thin layer starting at the external particle interface if the reaction rate is chemical reaction controlled.[6] Based upon the external surface area of the char particles,

$$\frac{dx}{dt} = k_s S_s p_{O_2}.$$

Here S_s is the specific external surface area of the particles and k_s is the chemical reaction rate constant based upon the external surface area of the reacting particles.

The reaction rate constant k_s has been developed for char by Field, et al.,[8] to be

$$k_s = A_o \exp(-\Delta E_a / RT_s)$$

where: $\Delta E_a = 35.7$ kcal/mol

$A_o = 8.71 \times 10^5 kg/m^2 \cdot s \cdot (MN/m^2)$.

When the reaction rate is limited by the diffusion of gases through the ash layer and/or the gas film on the particles, then the rate constant can be replaced by the factor $[(1/(1/k_{diff} + 1/k_s)]$.

Experimental evidence from previous investigators indicates that the reactivity of chars with oxygen in the chemical reaction control regime depends strongly upon the degree of gasification of the char. As the carbonaceous matter in a char particle is consumed by reaction with oxygen, a dramatic modification of the pore structure of the particle takes place. This pore structure phenomenon may well be the primary factor that determines the char reactivity with oxygen, thus masking major influences associated with the parent coal or the conditions of devolatilization under which the char was generated.

APPENDIX II

Multimedia Environmental Goals: MATE and EPC Concepts

APPENDIX II

MULTIMEDIA ENVIRONMENTAL GOALS: MATE AND EPC CONCEPTS

The achievement and maintenance of an acceptable (or quality) environment must from a practical viewpoint involve the establishment of maximum allowable concentrations of chemical contaminants in the air, water, and solid materials which constitute the natural environment. Such concentrations may be referred to as Multimedia Environmental Goals (MEG) values. Ambient level MEG values thus represent the concentrations of contaminants or degradation products in the ambient air, water, or solid materials below which unacceptable negative effects to the surrounding populations or ecosystems do not occur. Emission level MEG values are concentrations of contaminants or degradation products in emissions, effluents, or disposals representative of the control limits achievable through technology.

A Multimedia Environmental Goals project, which is an integral part of the environmental assessment methodology program currently being developed under the guidance of the Fuel Process Branch of IERL-RTP at the Research Triangle Park in North Carolina, has been concerned with the definition and quantitation of MEG values. A master list of chemical compounds has been compiled for study. More than 600 chemical substances and physical agents are included representing individual compounds, complex effluents/mixtures and nonchemical degradants (such as visual effects, subsidence, heat, and noise). Primary emphasis has been placed on contaminants from fossil fuels processes (particularly coal gasification and coal liquefaction). The primary selection criterion was that the substance be associated with fossil fuels processes. Secondary emphasis has been placed on substances for which federal standards or criteria exist or have been proposed, substances for which threshold limit values or lethal dose values have been reported, substances which have been identified as suspected carcinogens or substances which appear

on the EPA consent decree list. Additionally, substances may be included which are present in the environment as pollutants and/or have been identified as being highly toxic.

To organize the more than 600 master list entries, substances have been arranged into categories based on chemical functional groups for organic compounds and on the most important chemical element present for inorganic compounds. This categorization scheme emphasizes logical relationships between groups of substances so that each category is characterized by toxicologically and chemically similar substances. A total of 85 categories (26 organic and 50 inorganic compounds) have resulted. A MEG number was assigned to each of the compounds addressed, the first two digits of which represent the category.

Methods of detection for some of the compounds within a specific category are known to be similar. Analysis of such groups as a whole is in some cases practical for broad screening applications. Phenolic compounds are thus addressed collectively by water quality recommendations; hence, phenols are grouped as a category in the master list.

Emission level MATE values pertain to gaseous emissions to the land, aqueous effluents to water, and solid waste to be disposed to land. These goals may have as their bases technological factors or ambient factors. Technological factors refer to the limitations placed on the control levels by technology, either existing or developing. Since there is a relationship between contaminant concentrations and emissions and the presence of these contaminants in ambient media, it is imperative to consider ambient factors when establishing emission level goals. Ambient factors included in the project are minimum acute toxicity effluents (MATE) values, ambient level concentration (ALC) values and elimination of discharge (EOD) values. This categorization is shown in Table II-1. MATE values are concentrations of pollutants in undiluted emission streams that would not adversely affect those persons or ecological systems exposed for short periods of time. ALC values are permissible concentrations of pollutants in emission streams which, after dispersion, will not cause the level of contaminant in the ambient

TABLE II-1. MULTIMEDIA ENVIRONMENTAL GOALS

Emission Level MEG Values

I. Based on Best Technology
   A. Existing Standards
      a. New Source Performance Standards
      b. Best Available Technology
   B. Developing Technology
      Engineering Estimates (R&D goals)
II. Based on Ambient Factors
   A. Minimum Acute Toxicity Effluent Values
      a. Based on Health Effects
      b. Based on Ecological Effects
   B. Ambient Level Goals
      a. Based on Health Effects
      b. Based on Ecological Effects
   C. Elimination of Discharge Values
      Natural Background

Ambient Level MEG Values

I. Current or Proposed Ambient Standard or Criteria
   A. Based on Health Effects
   B. Based on Ecological Effects
II. Toxicity Based Estimated Permissible Concentration (EPC) Values
   A. Based on Health Effects
   B. Based on Ecological Effects
III. Zero Threshold Pollutants (EPC) Values
   Based on Health Effects

(Individual MEG values for each subcategory may be defined for air, water, and land (solid material) concentrations.)

receiving medium to exceed a safe continuous exposure concentration. EOD values are concentrations of pollutants in emission streams which after dilution will not cause the level of contaminant to exceed levels measured as "natural background."

Ambient level MATE values incorporate three categories of information to describe estimated permissible concentrations for continuous exposure. The three categories are: (1) current or proposed federal ambient standards or criteria; (2) toxicity values including both acute and chronic effects; and (3) carcinogenicity or teratogenicity values. The existence of thresholds for carcinogens, teratogens and mutagens has been widely debated and is still unresolved. Estimated permissible concentrations must still be defined, however, if goals representing acceptable environmental quality are to be achieved.

A methodology for evaluating and ranking pollutants for the purpose of environmental assessment has been developed that can be used to establish MEG values for a large number of compounds. The system requires certain empirical data which are extrapolated through simple models to yield estimated permissible concentration (EPC) values or minimum acute toxicity effluent (MATE) values. The methodology relates to ambient level goals and emission levels goals (hazard to human health or to ecology induced by short term exposure to emissions). It is recognized that there are several other criteria pertinent to the development of MEG values that have not been incorporated into the methodology thus far developed. Additional work, however, is ongoing. New research is needed before refined models of estimation can be developed to allow inclusion of such criteria as synergisms, antagonisms and other possible secondary pollutant associations.

Two types of estimated permissible concentration values are integrated through selected models. Empirical data concerning the effects of chemical substances for human health and the ecology are translated into a set of toxicity-based EPC values. Another set of EPC values is supplied by a system relating carcinogenic or teratogenic potential to medium concentrations considered to pose acceptable risks. Overall, the methodology

defines a total of 22 different kinds of EPC values, many of which are interrelated. The EPC values have been coded by subscript for easy identification as shown in Tables II-2 and II-3.

MATE values as emission level goals are analogous to EPC values as ambient level goals. The basic difference is that MATE values represent concentration limits in effluents, emissions, and discharges for short-term exposure whereas EPC values could be considered as lifetime continuous exposure values for the ambient environment. Fourteen different MATE values have been defined in the methodology. MATE values carry three subscripts: the first defines whether the value refers to air (a), water (w), or land (l); the second, whether the value refers to human health (h) or the ecological environment (e); and the third, which model was used to derive the value (numerical index). The MATE values that have been used in this study were obtained from the report "Multimedia Environmental Goals for Environmental Assessment," Volume 2, MEG Charts and Background Information (EPA-600/7-77-136b).

TABLE II-2. DERIVATION OF HEALTH BASED EPC'S

Data	Interrelationship	Specific EPC Derived
TLV or NIOSH Recommendation (occupational exposure)		EPC_{AH1}, EPC_{AC1}
LD_{50}, LD_{Lo}	TLV $\propto$ LD_{50}*	EPC_{AH2}
Bioassay data (carcinogen testing)		EPC_{AC2}
Bioassay data (teratogen testing)		EPC_{AT}
	$EPC_{WH} \propto EPC_{AH}$**	EPC_{WH1}
LD_{50}		EPC_{WH2}
	$EPC_{WC} \propto EPC_{AC}$**	EPC_{WC}
	$EPC_{WT} \propto EPC_{AT}$**	EPC_{WT}
	$EPC_{LH} \propto EPC_{WH}$	EPC_{LH}
	$EPC_{LC} \propto EPC_{WC}$	EPC_{LC}
	$EPC_{LT} \propto EPC_{WT}$	EPC_{LT}

*Handy, R., and A. Schindler, "Estimation of Permissible Concentration of Pollutants for Continuous Exposure," Environmental Protection Agency, Research Triangle Park, N.C. EPA-600/2-76-155, June 1976.
**Stokinger, E.H., and R. L. Woodward, "Toxicologic Methods for Establishing Drinking Water Standards," J. Am. Water Works Assn., 50, 515-529 (1958).

TABLE II-3. DERIVATION OF ECOLOGY BASED EPC'S

Data	Interrelationship	Specific EPC Derived
Air concentration causing an effect in vegetation		EPC_{AE}
LC_{50} or TLm		EPC_{WE1}
Tainting Level		EPC_{WE2}
Cumulative Potential		EPC_{WE3}
Application Factor*		EPC_{WE4}
Hazard Level*		EPC_{WE4}
	$EPC_{LE} \propto EPC_{WE}$	EPC_{LE}

*Value supplied in Water Quality Criteria.
Subscript Key: A (air); W (water); L (land); E (ecological effects); numbers refer to specific models.